Universidad Carlos III de Madrid

Department of ADVANCED MATERIALS

PROYECTO FIN DE CARRERA:

BEHAVIOUR OF Fe COATING OF Mg POWDER USING MECHANICAL MILLING PROCESS

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Proyecto realizado en conjunto con **Konju National University** (Corea del Sur)

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Guillermo Otaduy

ABSTRACT

In order to synthesize a thermally stable Mg powder as a desulfurizer of iron melts, pure Mg powder was coated by Fe powder, using a mechanical milling process.

Since there is a wide range of approaches to MA, behaviours such as the size, morphology and layer thickness were investigated as a function of milling condition. As the milling conducted from 30 min, to 1 h, 3 h, 5 h, 7 h, 10 h, 20 h, 23 h and 30 h, Fe particles began to stick on the surface of Mg powders.

The layer of Fe formed from 1 h milling was about 3,8μm thick and gradually thickened to be 6μm, 11μm and 15μm with increasing the milling time to 5 h, 10 h and 30 h, respectively. The surface of coated powder became more widespread after 10 h milling; appearing the first coating signals after 30min. Due to Fe resistance to coating, the layer composition was studied under electronic microscope, discovering an optimal milling time.

NOMENCLATURE

AMPL	Advanced Material Processing Laboratory
EDS	Energy-dispersive X-ray spectroscopy
HB	Brinell Hardness
HEBM	High Energy Ball Milling
ICDD	International Centre of Diffraction Data
IM	Ingot Metallurgy
INCO	International Nickel Company
KNU	Kongju National University
LEBM	Low Energy Ball Milling
MA	Mechanical Alloying
ODS	Oxide Dispersion Strengthened
OM	Optical Microscope
PVD	Physical Vapour Deposition
SEM	Scanning Electron Microscope

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"*Success consist of going from failure to failure without loss of enthusiasm*"
Winston Churchill

1. INTRODUCTION

It is interesting how some of the most original inventions have been discovered as a by-product of a research into a different subject. The process of mechanical alloying is not safe from this statement.

Materials are probably more deep-seated in our culture than most of us realize. Transportation, housing, clothing, communication, recreation and food production – virtually every segment of our everyday lives is influenced to one degree or another by materials.

Sometimes, it is useful to subdivide the discipline of materials science and engineering into *material science* and *materials engineering* sub disciplines. Strictly speaking, "materials science" involves investigating the relationships that exist between the structures and properties of materials. In contrast, "materials engineering" is, on the basis of this structure–property correlations, designing or engineering the structure of a material to produce a predetermined set of properties.

From a functional perspective, the role of a material engineering is to create and develop new products or systems using existing materials, and/or develop techniques for processing materials.

On the present research, the investigation was focused on the idea of developing a new product, out of existing and common materials, for an intended purpose. This material will be made from the mixture of two metallic elements, making an alloy.

1. 1. METAL ALLOYS

If there is a typical material that is associated in the public´s mind with modern engineering practice, it is structural steel, a metal alloy.

An alloy is a metal composed of more than one element. Engineering alloys include the cast irons, and steels, aluminium alloys, magnesium alloys, titanium alloys, nickel alloys, zinc alloys, and copper alloys.

Most alloys are created to change the elemental metal's physical properties, such as conductivity, density, ductility, hardness, malleability, melting point, tensile strength, and/or chemical properties, such as resistance and corrosion.

A very common classification of metallic alloys is the one that divides it in ferrous and non-ferrous alloys.

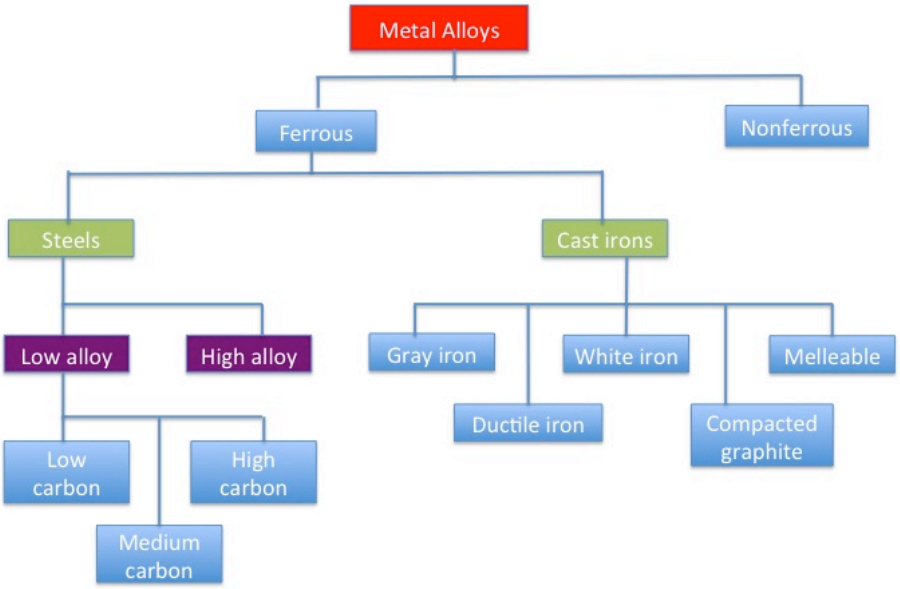


Figure 1 Classification scheme for the various ferrous alloys [1]

Rarely do we find metallic elements in their "free" state. Industry gets its metals from an ore, the pure elements are not found in nature. Ores are often a combination of the metallic element and a non-metallic element.

1.1.1 FERROUS ALLOYS

Ferrous alloys, those in which iron is the principal constituent, include steel and cast irons. The difference between steel and cast irons is the quantity of carbon contained in the metal. Pure iron is a soft metal made up of ferrite crystals.

The existence of ferrous alloys is possible due to the iron ores, which are rocks and minerals from which metallic iron can be economically extracted. This ores, have a composition rich in iron oxides, and the amount of iron in them varies up to 70%.

Iron ore is the raw material used to make pig iron, which is one of the main raw materials to make steel, 98% of the mined iron ores used to make steel. It has been argued that iron ore is "more integral to the global economy than any other commodity, except perhaps oil" [2].

Iron is the world's most commonly used metal – steel, of which iron is the key ingredient, representing almost 95% of all metal used per year.

Fabrication processes alter alloy properties, and in addition, further property alterations may be induced by the employment of appropriate heat treatments. The alloy studied on this research is meant for use on the fabrication period, were the sulphur in the iron melt should be removed.

a. Smelting process

Iron is produced from iron ore in a blast furnace. The commercially important iron ores are oxides such as haematite (Fe_2O_3) and magnetite (Fe_3O_4).

Iron ores consists of oxygen and iron atoms bonded together into molecules. To convert it to metallic iron it must be smelted or sent through a direct reduction process to remove the oxygen. Oxygen-iron bonds are strong, and to remove the iron from the oxygen, a stronger elemental bond must be presented to attach to the oxygen [3].

Carbon is used because the strength of a carbon-oxygen bond is greater than that of the iron-oxygen bond, at high temperatures. Thus, the iron ore must be powdered and mixed with coke, to be burnt in the smelting process.

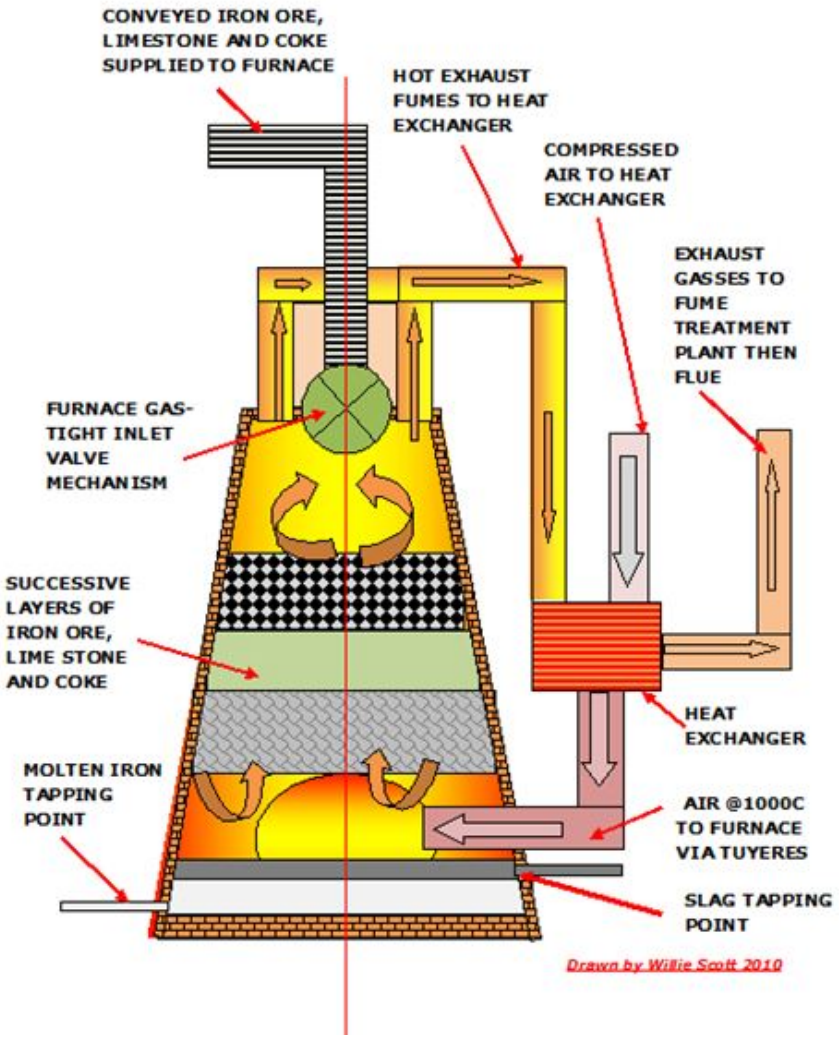


Figure 2 Iron furnace by Willie Scott

Coke is used on the blast furnace as a source of heat for the smelting operation. Limestone is added, which acts as a flux to combine with the iron-poor materials on the ore, forming a slag, and thereby removing them from the iron itself.

This liquid slag floats on the top surface and is tapped off. The molten iron is the heaviest substance in the furnace. It sinks to the bottom, or the hearth, where it is also tapped off into ladles, known as pigs.

During the smelting process, the iron absorbs various quantities of carbon, silicon, sulphur, phosphorus, and manganese, which are all present in the pig iron.

The amount and form of carbon present is the distinguishing difference between cast iron and steel.

The inclusion of even small amounts of some elements can have profound effects on the behavioural characteristics of a batch of iron or the operation of a smelter. These effects can be good and bad, some catastrophically bad.

Some chemicals are deliberately added such as flux, which makes a blast furnace more efficient. Others are added because they make the iron more fluid, harder, or give it some other desirable quality.

b. Chemical Composition

Ideally iron ore contains only iron and oxygen. In reality this is rarely the case. Typically, iron ore contains a host of elements, which are often unwanted in modern steel.

- Silicon: Silica (SiO_2) is almost always present in iron ore. Most of it is slagged off during the smelting process. At temperatures above 1300 °C some will be reduced and form an alloy with the iron. The hotter the furnace, the more silicon will be present in the iron. The major effect of silicon is to promote the formation of grey iron. Grey iron is less brittle and easier to finish than white iron.
- Phosphorus (P): Has four major effects on iron: increased hardness and strength, lower solidus temperature, increased fluidity, and cold shortness. Depending on the use intended for the iron, these effects are either good or bad.
- Aluminium (Al): Is often present in the form of clay, or in the limestone. Al is very hard to reduce, therefore is not a problem. However, it does affect the slag, defaulting its operation.
- Sulfur (S): Is often concentrated in the coal, and also in the ore in small quantities. The effects of even small amounts of sulfur are immediate and serious. Sulfur causes iron to be red or hot short. This makes the iron brittle and reduces its mechanical properties especially at high temperatures, which makes it difficult to work on it. Today, it is possible to work the hot short iron at low temperatures, but it requires an incredible amount of extra-energy. The degree of hot shortness will depend on the amount of sulfur.

The manufacture of high-quality ductile iron begins with the careful selection of charge materials that will give a relatively pure cast iron, free of the undesirable residual elements sometimes found in other cast irons. Carbon, manganese, silicon, phosphorus, and sulfur must be held at specified levels. Alloys are controlled to the extent needed to obtain the required mechanical properties, and/or microstructure in the critical sections of the casting.

c. *Desulfurization*

During the past decades the requirements regarding the sulfur content in liquid iron melts have become more and more severe and will most probably continue to increase. Such iron melts are, for example, liquid pig iron used for casting purposes such as white and grey cast iron, or nodular cast iron.

Desulfurization of pig iron and steel has taken on increasing importance because ores of lower quality and increasingly higher sulfur containing coke or heating oil are used. Also, the ever-increasing demands in regard to the properties of various kinds of alloys, which frequently can be met only when extremely low sulfur contents are obtained.

Over the years that iron has being extracted, there have been many ways of reducing the amount of sulfur. It has been done to the iron ore by roasting and washing, and other ways such as in the pig iron melts. A wide range of materials and methods that lead to satisfactory levels of desulfurization are known, but an every day search for the most economic most effective method is taking place.

This research will focus on the creation of a metallic alloy agent formed by Fe and Mg. The object is to create a solid desulfurization agent, which on a future study will be introduced into the iron melt.

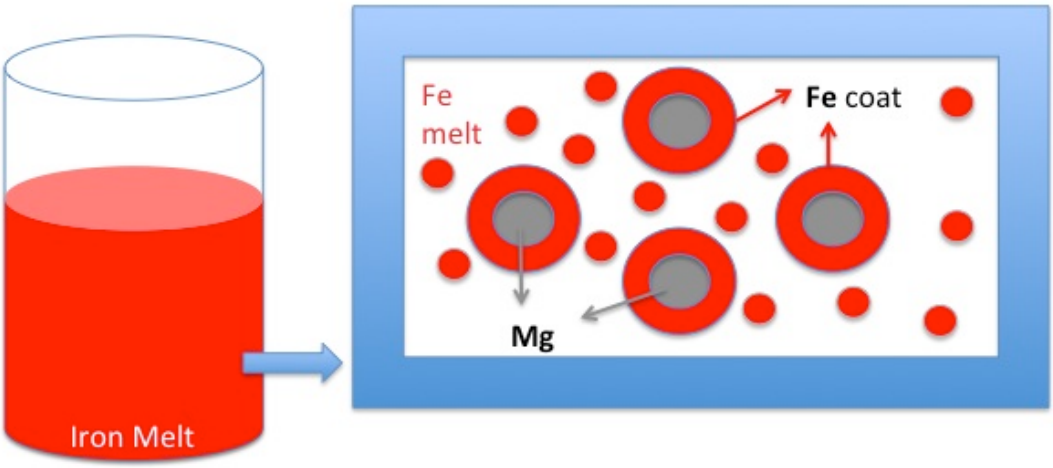


Figure 3 Desulfurization agent inside iron melt

Due to the different melting temperatures, and boiling temperatures, it is not possible to introduce Mg powder into the iron melt, without its fast evaporation.

Fe melting Temperature = 1811ºK = 1538 ºC
Mg melting Temperature= 923 ºK = 650 ºC
Mg boiling temperature= 1363 ºK = 1091 ºC

If an Iron shield covers the magnesium particles, they can be introduced into the iron melt, without expecting to boil and evaporate rapidly. When the

magnesium evaporates, it gets hold of some sulfur, but less than if it was in liquid state mixed with the melt.

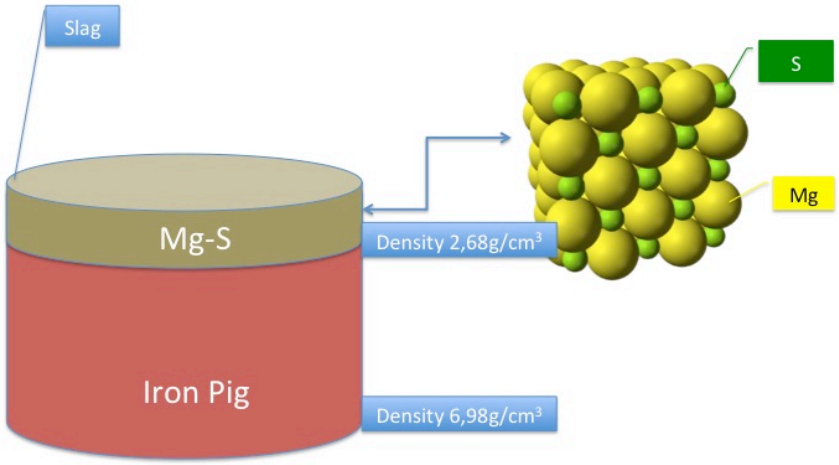


Figure 4 Sample of the wanted scene

The object is to remove afterwards the magnesium sulfide, which could be found at the top layer, due to its difference in density with de iron, which is much heavier.

The way to create the desulfurization agent is through mechanical alloying. The research will target on the creation of an iron coat for the magnesium particles through mechanical alloying.

1.1.2 TYPES OF ALLOY

There are three ways in which a metal might respond to the addition of another element. The first, and probably the simplest, response occurs when the two materials are insoluble in one another in the solid state. In this case the base metal and the alloying addition each maintain their individual identities, structures, and properties. The alloy in effect becomes a composite structure, consisting of two types of building blocks in an intimate mechanical mixture.

The second possibility occurs when the two elements exhibit some degree of solubility in the solid state. The two materials can form a solid solution, where the alloy element dissolves in the base metal. The solutions can be: substitutional or interstitial. In the substitutional solution, atoms of the alloy element occupy lattice sites normally filled by atoms of the base metal. In an interstitial solution, the alloy element atoms squeeze into the open spaces between the atoms of the base metal lattice [17].

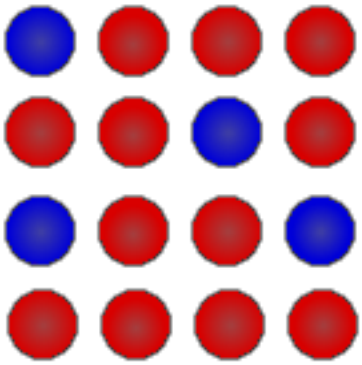


Figure 5 Substitutional alloy

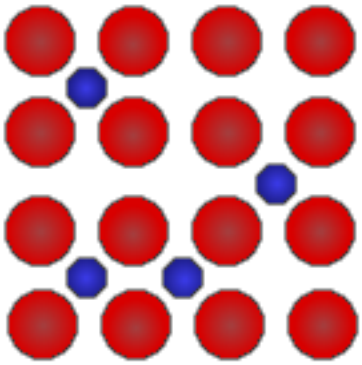


Figure 6 Interstitial alloy

A third possibility exists, where the elements combine to form intermetallic compounds. In this case, the atoms of the alloying element interact with the atoms of the base metal in definite proportions and in definite geometric relationships. The bonding is primarily of the non-metallic variety, and the lattice structures are often quite complex. Because of the type of bonding, intermetallic compounds tend to be hard, but brittle, high-strength materials.

Even though alloys are composed of more than one type of atom, their structure is still one of crystalline lattices and grains. Their behaviour in response to applied loadings is similar to that of pure metals, with some features reflecting the increased level of structural complexity. Dislocation movement can be further impeded by the presence of unlike atoms. If neighbouring grains have different chemistries and/or structures, they may response differently to the same type and magnitude of load.
On the present research, the intention is to create an alloy where each element maintains its original structure and properties, for the further purpose of sulphur removal; it is necessary that the Mg keep its identity.

1.2 MECHANICAL ALLOYS

Mechanical alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing, and re-welding of powder particles in a low-, medium-, or high-energy mill. It is a powder processing technique that allows production of homogeneous materials starting from blended elemental powder mixtures [5].

Originally developed to produce oxide-dispersion strengthened (ODS) nickel- and iron-base super-alloys for applications in the aerospace industry, MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium phases starting from blended elemental or pre-alloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys [5].

The technique of MA to synthesize novel alloy phases and to produce oxide dispersion strengthened materials has attracted the attention of a large number of researchers during the past 10 years.

To obtain the desired alloy, composed by Mg and Fe, the method used will be mechanical alloying. The mixture of these two compounds will be milled, in order to obtain a homogeneous alloy.

1.2.1 THE PROCESS

The actual process of MA starts with mixing of the powders in the right proportion and loading the powder the powder mix into the mill along with the grinding medium steel balls. This mix is the milled for the desired length of time, until a steady state is reached when the composition of every powder particle is the same as the proportion of the elements in the starting powder mix.

The important components of the mechanical alloy process are the raw materials, the mill and the process variables, which will be discussed briefly in the following notes.

a. Raw Materials

The raw materials used for MA are widely available commercially pure powders that have particle sizes in the range of 1-200μm normally. But the powder particle size is not very critical, except that is should be smaller than the grinding ball size..

b. Types of Mills

Different types of milling equipment are used to produce mechanically alloyed powders. They differ in their capacity, efficiency of milling and additional arrangements for cooling, heating, etc. The different mills available are:

- SPEX shaker mills
- Planetary ball mill, Figure 6.
- Attritor mills
- Commercial mills
- New designs: For specialized purposes.

Figure 6 Planetary ball mill. - Pulverisette 6 (Fritsch)

The planetary ball mill owes its name to the planet-like movement of its vials. These are arranged on a rotating support disk and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the vials rotating around their own axes, and the one produced by the rotating support disk, both act on the vial contents; raw material to be ground and the grinding balls.

Since the vials and the supporting disk rotate in opposite directions, the centrifugal forces alternately act in identical and opposite directions. This causes the grinding balls to run down the inside wall of the vial (the friction effect), followed by the material being ground, and grinding balls lifting off and traveling freely through the inner chamber of the vial to bump against the opposing inside wall (the impact effect) [5].

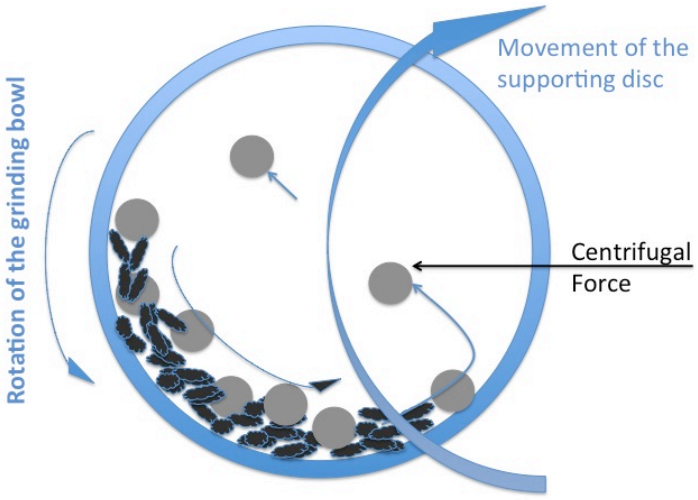


Figure 7 Schematic depicting the ball motion inside the ball mill

In the modern versions, it is possible to control the disk and the vial rotation speeds.

c. Process Variables

Mechanical alloying is a complex process and hence involves optimization of a number of variables to achieve the desired microstructure. All these variables are not completely independent, for example, the optimum milling time depends on the type of mill, size of the grinding medium, etc.

Some of the important parameters that have an effect on the final constitutions of the powder are:

1.2.1.c.1 Milling Container:

The material used for the milling container is important since due to impact of the grinding medium on the inner walls of the container, some material will be dislodged and get incorporated into the powder. This can contaminate the powder or alter the chemistry of the powder. If the material of the grinding vial is different from that of the powder, then the powder may be contaminated with the grinding vial [5].

1.2.1.c.2 Milling Speed:

The faster the mill rotates the higher would be the energy input into the powder. But, depending on the design of the mill, there are certain limitations to the maximum speed that could be used. For example, in a conventional ball mill increasing the speed of rotation will increase the speed with which the balls move [5].

There is a critical speed, where the balls will be pinned to the inner walls of the vial and do not fall down to exert any impact force. Therefore, the maximum speed should be just below this critical value so that the balls fall down from the maximum height to produce the maximum collision energy.

Another limitation of the maximum speed is that at high speeds, the temperature of the vial may reach a high value. This may be advantageous in some cases where diffusion is required to primate homogenization, but in other cases this may be a disadvantage, because it may accelerate the transformation process and results in the decomposition of supersaturated solid solutions, and also may contaminate the powders.

1.2.1.c.3. Milling Time:

The time of milling is the most important parameter. Normally the time is so chosen as to achieve a steady state between the fracturing and cold welding of the powder particles. The times required vary depending on the type of mill used, the intensity of milling, the ball-to-powder ratio, and the temperature of milling.

These times have to be decided for each combination of the above parameters and for the particular powder system. But, it should be realized that the level of contamination increases and some undesirable phases form if the powder is milled for times longer than required, that it is why is would be desirable that the powder is milled just for the required duration and not any longer.

1.2.1.c.4. Grinding Medium:

The most common types of materials used for the grinding medium are the different varieties of steel. This grinding medium should have enough density to create a sufficiently high impact force on the powder. It is always desirable to have the grinding medium and the grinding vial made of the same material as the powder, so that there would be no risk of cross contamination, however, this is impossible in most of the cases.

The size of the grinding medium has also relevancy in the efficiency of the milling. Normally, a large size and high density of the grinding medium should be useful due to the higher weight of the balls would transfer more impact energy to the powder particles.

1.2.1.c.5. Ball-to-powder weight Ratio:

The BPR is an important variable in the milling process. The BPR has a significant effect on the time required to achieve a particular phase in the powder being milled. Some investigators discover that the higher the BPR, the shorter is the time required, because of an increase in the weight proportion of

the balls, the number of collisions per unit time increases and consequently more energy is transferred to the powder particles and so alloying takes places faster, however this could also be due to the increase in temperature caused by the higher heat generation [5].

1.2.1.c.6. Milling Atmosphere:

The major effect of the milling atmosphere is on the contamination of the powder. Therefore, the powders are milled in containers that have been either evacuated of filled with an inert gas such as argon or helium.
High purity Argon is the most common ambient to prevent oxidation and/or contamination of the powder. The type of atmosphere also seems to affect the nature of the final phase.

1.2.1.c.7. Temperature of Milling:

The temperature of milling is another important parameter in deciding the constitution of the milled powder. Since diffusion processes are involved in the formation of alloy phases, it is expected that the temperature of milling will have a significant effect in any alloy system [5].

Depending on all of these variables, the final product obtained after application of the mill, will be different. It will be the key point in order to generate the perfect powder, to arrange the optimal conditions.

2. HISTORY AND STATE OF ART

"*… the history of the development of machines may be retraced by the the history of the flour mill*" Karl Marx (Kuprits 1967).

Chimpanzees in some regions of West Africa have a culture of nut cracking that may extend back 2.6 million years [6]. Size reduction, can be considered the oldest engineering process. It has its beginnings in prehistoric times, when early humans pounded grains and nuts with stones to free the edible inner parts from the hard protective shells. The mortar and pestle, a combination of bowl-shaped container (the mortar) and a rod with flat-surfaced hammer (the pestle), was the earliest tool used for this task, and in principle, has remained unchanged throughout the ages.

Over centuries the technologies have evolved, urged by the needs of new performance. The millstones and querns were useful until greater forces were needed, when mineral ores were worked. With the metal revolution also came new needs, new inventions. The old methods led the way for new, like the water-driven stamp mills for grinding and the windmills. Throughout the history of size reduction, innovation has been driven mainly by technological advances associated with energy and with new materials.

The evolution of machines from devices driven by one person to immense machines with capacities of many hundred tons per hour has followed the path of technology in general.

Table 1 The progress of size reduction technology [6]

Stages in Technology Development	**Factors interacting at each stage**
Human muscles	Available materials
Men or animals working together	Accumulated skills and experience
Waterpower	Economic and social conditions
Steam power	Religious and ethical tenets
Electricity	Philosophical doctrines
Energy Available per Machine	**Power Delivered by muscles ft-lb/sec**
Stone age- Human muscles: 0,1KW/person 600BC- Men or animals working together: 0,5KW	Draft horse: 432 Ox: 288
100BC- Water wheel: 5KW	Mule: 216
1800- Steam engine: up to 50KW	Donkey: 108
1900- Electricity: No limit	Human pumping: 33 Human winching: 45

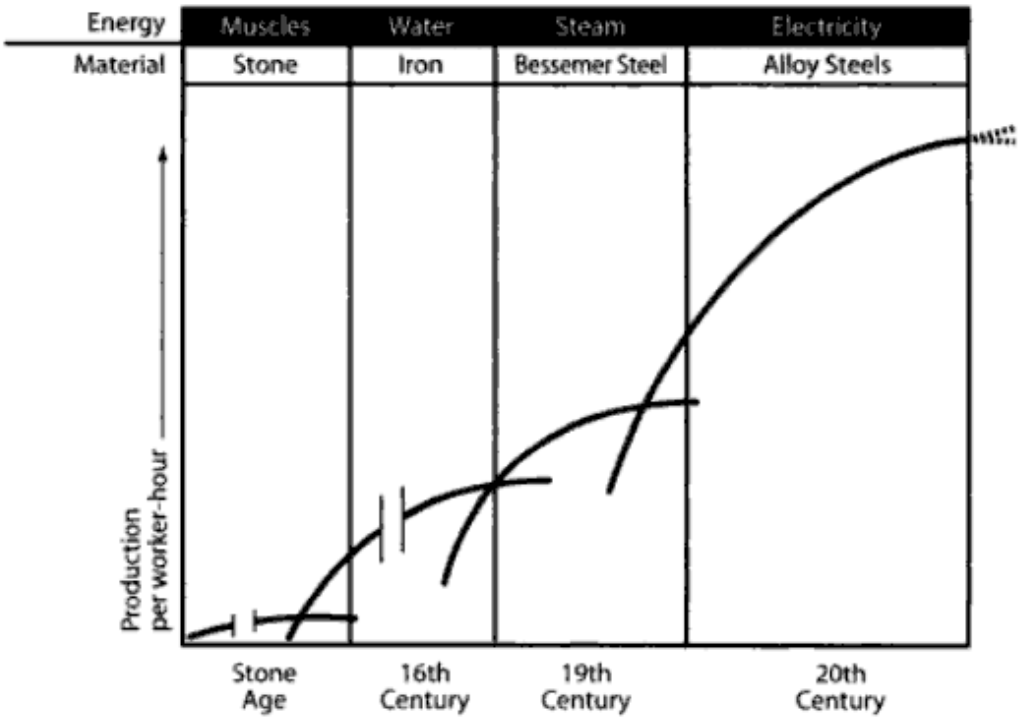


Figure 8 Effects on energy sources and materials on size-reduction processes [6]

Size reduction is not only the most ancient technology; it is also the most widespread. It is used in every country and in every industry that involves solid particles. Here are some important applications [6]:

- Breaking wheat grain to separate endosperm from bran and grinding the endosperm to produce flour.
- Grinding many foodstuffs, including spices, confectionery and animal foods.
- Breaking rock masses into boulders and pebbles.
- Crushing and grinding ores to produce copper, iron, gold and other metals.
- Pulverizing coal to combust in power stations.
- Grinding limestone and clinker to make cement.
- Grinding industrial minerals to use as pigments and to manufacture fertilizers, glass, chemicals, pharmaceuticals, and many other products.

Devices for shaking materials along with hard balls might be old, but it was not until the industrial revolution and the invention of steam power that a machine could be built.

The recent ball mills are machines capable of a size reduction up to a few microns. The ball mill is a type of grinder used to grind materials into extremely fine powder for use in many areas, including material engineering.

However, ball mills are used extensively in mechanical alloying processes, in which they are used for grinding and mixing, at high energies produces cold welding as well as fracture, which was named “mechanical alloying” by Ewan C. MacQueen, a patent attorney for the International Nickel Company [18].

Mechanical alloying (MA) is a solid-state powder processing technique involving repeated cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill [7]. The transfer of mechanical energy to the power particles results in introduction of stain into the powder though generation of dislocation and other defects, which act as fast diffusion paths. Additionally, refinement of particle and grain size occurs.

It is not imprudent to believe that this advanced technique of material manipulation has its part of origin and nature related with the ancient techniques of size reduction, in principal, it has the same procedure; to hit grains with harder materials, however, MA alloying purposes and processes are far from been as simple as a size reduction technique.

2.1 MECHANICAL ALLOYING

W.D Coolidge first exploited the use of inert additions to improve elevated temperature mechanical properties of metals in 1910 in thoriated tungsten. The development of dispersion-strengthened alloys by internal oxidation started in 1930 and the invention of dispersion-strengthened aluminium was a severe limitation for use of SAP at elevated temperatures. This led to attempts in applying dispersion strengthening to higher melting point metals such as Copper and Nickel [10].

John Benjamin and his colleagues at the Paul D. Merica Research Laboratory of the International Nickel Company (INCO) developed the process around 1966. The technique was the result of a long search to produce a nickel-base super-alloy, for gas turbine applications, that was expected to combine the high temperature strength of oxide dispersion and the intermediate-temperature strength of gamma-prime precipitate. The required corrosion and oxidation resistance was also included in the alloy by suitable alloying additions. Benjamin had summarized the historic origins of the process and the background work that led to the development of the present process [8].

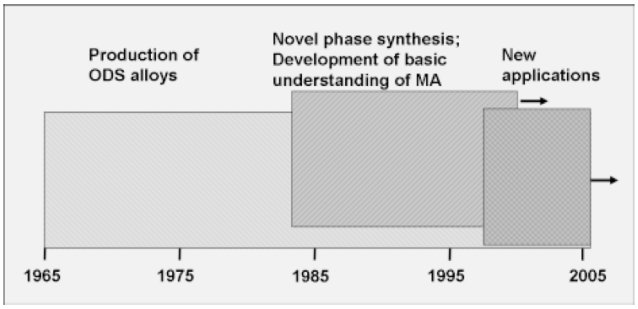


Figure 9 Schematic showing the different periods of development in MA since its inception in 1966 [11]

The development of this technique has enabled a huge diversification. As explained, its original practice was to produce a mixture with the ODS, but over the years its applications have multiplied, been nowadays a current procedure for many material making.

Mechanical alloying is normally a dry, high-energy ball milling technique and has been employed to produce a variety of commercially useful and scientifically interesting materials. Because some of the special attributes on Table 2, this simple but effective, processing technique has been applied to metals, ceramics, polymers, and composite materials.

Table 2 Attributes of mechanical alloying [8]

Attributes of Mechanical Alloying
Production of fine dispersion of second phase (usually oxide) Particles
Extension of solid solubility limits
Refinement of grain sizes down to nanometer range
Synthesis of novel crystalline and quasicrystalline phases
Development of amorphous (glassy) phases
Disordering of ordered intermetallics
Possibility of alloying of difficult to alloy elements
Inducement of chemical (displacement) reactions at low temperatures
Scaleable process

Mechanical alloying, the innovation of Benjamin forty years ago, has changed the traditional method in which production of materials is carried out by high temperature synthesis. It has attracted much attention and inspired numerous research interests because of its promising results, wide possible applications and potential scientific values. MA has now been recognized as a unique technique. It has been utilized in different areas of material processing and applied to many different material systems. ODS materials, composites, amorphous, nanocrystalline alloys, intermetallic compounds, non-equilibrium materials and ceramics have all been successfully synthesized, an achievement not possible by means of traditional techniques [9].

Today, MA has been used for developing alloys from immiscible liquids or solids, incongruent melting, intermetallic and metastable phases, and has emerged and developed into a technology capable of providing unique PM materials with consistent properties for high performance applications over a wide range.

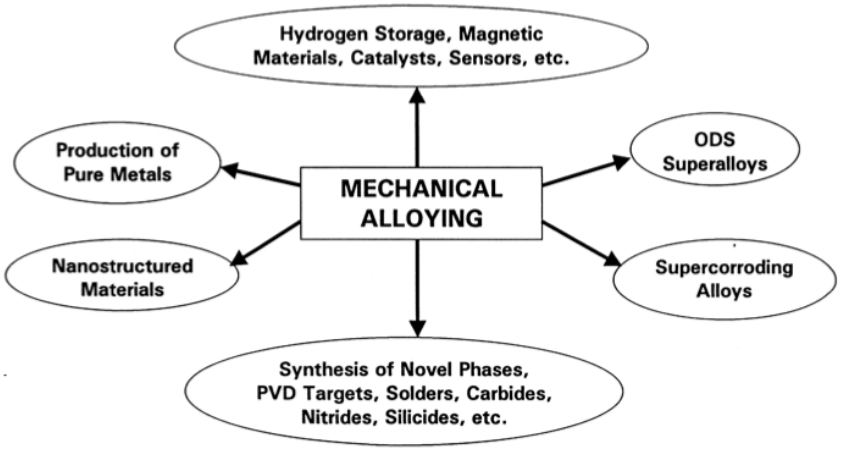


Figure 10 Typical current and potential applications of mechanically alloyed products [12]

2.2 PRESENT APPLICATIONS

The most important application of mechanically alloyed products is in the form of ODS alloys. These alloys have complex compositions and it is difficult to process them through conventional ingot metallurgy (IM) methods.

Mechanically alloyed materials are strong both at room and elevated temperatures. The elevated temperature strength is derived from more than one mechanism. The very homogenous distribution of alloying elements during MA gives both the solid solution strengthened and precipitation-hardened alloys more stability at elevated temperatures and overall improvement in properties.

Apart from ODS alloys, the technique of MA is also being commercially used to produce PVD targets for the electronic industry. This is because it is easier to produce a chemically homogeneous product by MA rather tan IM methods.

Yet another commercial application of mechanically alloyed products (which has its relevancy for the use of same raw materials to the present study) is in the use of the MRE (meal ready-to-eat). These heaters contain finely ground mechanically alloyed powders of Mg and Fe, which on contact with water produce heat [13].

Recently, is has also been reported that Zoz in Germany and Fukuda Metal Foil and Powder in Japan have joined together in producing a mechanically alloyed material for paints and solders [14].

The most important advantage of MA in all these applications is in the production of highly homogeneous product without any segregation effects being present in them.

3. GOAL

The goal of this research is the Fe coating of Mg powder, targeting the later introduction into iron melts.

The method used to achieve this purpose is mechanical alloying. Ball mills are used extensively in the mechanical alloying process, in which they are responsible of grinding, cold-welding and powder refinement as well. In order to achieve the goal, the Fe must weld around the Mg particles, forming a coating that in future will protect the inside from high temperatures when introduced in melt.

The development of the desired microstructure is what will focus the researches detailed study, considering coat thicknesses, composition, surface and the distribution on particle size.

It is also pretended on this research to approximate these techniques to the non-specialized readers, been witnesses of the detailed material manipulation following MA principles in order to obtain the required alloy.

4. EXPERIMENTAL PROCESS

With the object to study the microstructure of a mechanical alloyed powder, and achieve the goal, a frame wide enough was set to encourage for possible alternatives. With this reason in mind, the experiment would have to begin from lowest energetic option available, in order to narrow every possible direction with experimental results as a guide.

Reasonably, during the experimental processes a lot of data was gathered, some will be explained onwards in detailed examination, and other only mentioned.

As in every experiment is required, the very first step is to have a clear idea of what is expected to obtain, and what procedure will be followed (how to achieve it), and then start gathering the products needed, the materials, then it is necessary to select the equipment, and finally, depending on the equipment used, the variables of the process.

It is also highly important to meditate before starting the methodical procedure, how the results will be analysed. Depending on this matter, sometimes it is better to conduct the experiment in one direction or other.

4.1 RAW MATERIALS

The raw materials used for MA are widely available commercially pure powders that have particle sizes in the range of 1-1000μm.

But the powder particle size is not very critical, except that is should be smaller than the grinding ball size, as it was explained introduction. The powder of Fe is easily found. Fe is the most commonly used metal, representing up to 95% of all metal used per year. In the present research it was used an Fe powder with a particle size of 180μm.

Figure 11 Fe powder photograph from laboratory

Fe, a material represented in the periodic table as a transition metal, among other properties is a widely known ferromagnetic metal:

Fe Powder	
Grain Size	180μm
Crystalline Structure	BCC
Density (g/cm3)	7,874
Liquid density (g/cm3)	6,98
Melting Temperature (K)	1811
Boiling Point (K)	3114
Brinell Hardness (Mpa)	460
Young's Modulus (Gpa)	211

The other powder used in the research was magnesium, which is also an easy material to find nowadays, as the 11th most abundant material on earth. The particle size of the Mg powder used was of 700μm. Unusually high, but suitable for our experimental conditions.

Figure 12 Mg Powder photograph from laboratory

The Mg is represented in the periodic table as an alkaline earth metal. It is also known for been a paramagnetic metal:

Mg Powder

Grain Size	700µm
Crystalline Structure	HCP
Density (g/cm3)	1,738
Liquid density (g/cm3)	1,584
Melting Temperature (K)	923
Boiling Point (K)	1363
Brinell Hardness (Mpa)	260
Young's Modulus (Gpa)	45

Take notice of how the Mg is much lighter than the Fe, which is one important characteristic in order to understand the future process of desulfurization along with the temperatures, main cause of the problem. At the temperature where Fe starts to melt, the Mg evaporates.

It is very important to fix the quantity of raw material used. During all experiments; LEBM and MEBM, it was fixed the same amount of powder, 20grams, with the same relation between different powders. The relation is 7:3, Mg to Fe. In every sample was used 14grams of Mg and 6grams of Fe. With this settled, the next step consists on deciding the equipment and the variable conditions.

4.2 EQUIPMENT

The equipment that has been used in this research is the available in the AMPL of Konju National University.

4.2.1.MILL

In order to develop the mechanical alloyed samples needed, it was decided to use a ball-milling device. Through all the experiment, it was necessary to use two different types of mill, to obtain the desired microstructure.

One of the mills used, was the WiseMix Ball Mill. It is considered throughout this research as a type of LEBM.

Figure 13 LEBM: WiseMix Ball Mill

This mill can achieve a velocity up to 600rpm.

The other mill used for the research was the Pulverisette 6, from Fritsch. Design with only one grinding bowl mount operates according to the principle of the planetary ball mills. In comparison to the capacities that the new mills are developing, the mill used could be said to be a “medium energy” ball milling.

Figure 14 Pulverisette 6 (Fritsch)

The Pulverisette 6 has a main disc speed from 100 to 650 rpm, and has a maximum sample capacity of 225ml.

4.2.2. VACUUM CHAMBER

For the MA process, it was decided to make an Argon atmosphere, so that energy transmitted to the particles during the milling would not conduct to contamination or oxidation of the powder.

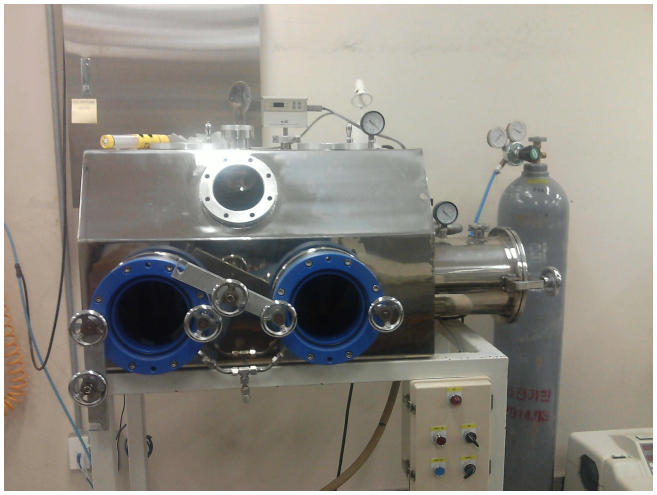


Figure 15 Argon vacuum chamber

4.2.3. X-RAY DIFFRACTOMETER

Inside KNU facilities, there are a number of laboratories with high precise equipment. The SMD 3000 from SCINCO offers a wide range of analytical requirements, from a routine qualitative and quantitative analysis, to residual-stress, crystal size and lattice strain. In this research it was use for high resolution XRD.

Figure 16 X-Ray Diffractometer SMD3000 from SINCO

Powder diffraction is a technique used to characterize the crystallographic structure, and preferred orientation in powder solid samples. Is commonly used by comparing diffraction data against a database maintained by the ICDD. The SMD 3000 has a cupper metal target anode inside an evacuated x-ray tube. Due to the Cu target metal, the suitable operating conditions selected were 40kV and 40mA.

2.3.4. OPTICAL MICROSCOPE

The main purpose of a microscope is to reveal the microstructural details in specimens that are too small to be seen with the naked eye. An OM consists of three important components –illumination system, objective, and eyepiece. Using any microscope, it will be possible to observe the microstructure.

Figure 17 Optical Microscope OLYMPUS BX41M

The AMPL has an OM from OLYMPUS, the BX41M (Figure 17). It was used to analyse all MA powders through detailed observation. The power is turned on, and with the white help of a transformer, the brightness of the light may be adjusted. The specimen has been prepared for observation is placed on the stage of the microscope with the polished and etched surface facing the objective lens.

2.3.5. SCANNING ELECTRON MICROSCOPE (SEM)

A SEM is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons, in a raster scan pattern. Unlike the optical microscope, which had been discussed earlier, the source of illumination in the SEM is an electron beam.

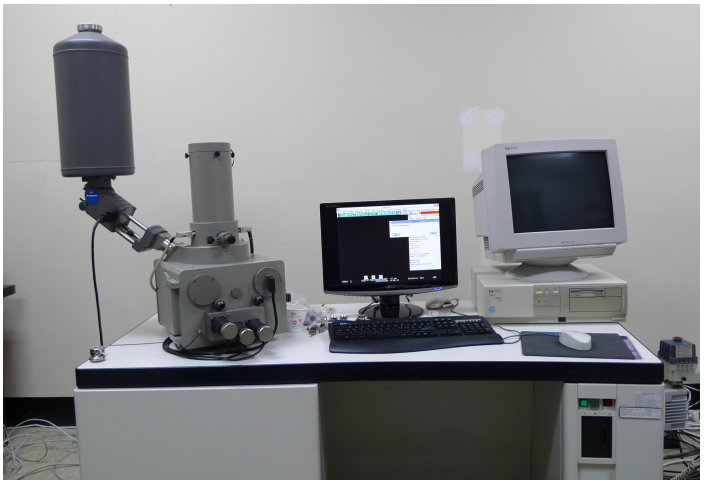


Figure 18 AMPL SEM from LEICA Cambriedge LTD

In this study it was used a SEM with an OXFORD Pentafet X-Ray detector integrated in a LEICA-Cambridge electron microscopy. The SEM is capable of producing much higher magnifications and lower limits or resolution than is possible in an optical microscope.

The microscope was used for making the EDS of various specimens, where it is possible to determine the chemical composition of the different phases, both quantitatively and qualitatively.

4.3. PROCESS VARIABLES

Once all the equipment is settled, it is time to fix a number of process variables. In order to obtain the desired structure, an iron-coated magnesium powder, the variables and conditions were set depending on the machine used.

4.3.1. LOW-ENERGY BALL MILLING

- Milling Container: The AMPL provided with a zirconium milling jar, with 56mm of diameter.

Figure 19 Zirconium Milling Jar

- Grinding Medium: In order to use with the provided zirconium jar, it was considered necessary to use zirconium-grinding balls. The balls had a diameter of 2mm.

Figure 20 Set of materials for LEBM

- Ball to powder weight ratio: The ratio was set up for 10 to 1. Ball (10), powder (1). During all experiments, the quantity 20grams of powder for 200grams of grinding medium could work fine to obtain the desired microstructure.

- Milling atmosphere: All the samples were conducted in an Argon atmosphere.

- Milling Speed: The LEBM was set for a maximum speed of 300rpm.

- Milling Time: In order to obtain a variety of samples to compare and obtain valuable information, a decision was made to set a wide gap of time between three different measures; 30min, 10hours and 30hours.

- Temperature of Milling: The temperature was not controlled. In every sample fabricated, the temperature was free for variation.

4.3.2. MEDIUM-ENERGY BALL MILLING

- Milling Container: The AMPL provided a stainless steel milling cylindrical container, with 10 cm of diameter. It would be necessary to take it into consideration if the contamination of the powder takes place.

Figure 21 MEBM container

- Grinding Medium: The AMPL provided stainless steel grinding balls with a total ball diameter of 3,2mm.

Figure 22 MEBM grinding medium

- Ball to powder weight ratio: The ratio was set up for 10 to 1 as in the LEBM. Ball (10), powder (1).

- Milling atmosphere: All the samples were conducted in an Argon atmosphere.

- Milling Speed: The MEBM was set for a maximum speed of 600rpm.

- Milling Time: In order to obtain a higher variety of samples, it was decided to make a collection MA powder for 30min, 1 hour, 90min, 2 hours, 3 hours, 4 hours, 5 hours, 7 hours, 10 hours, 20 hours, 23 hours and 30 hours.

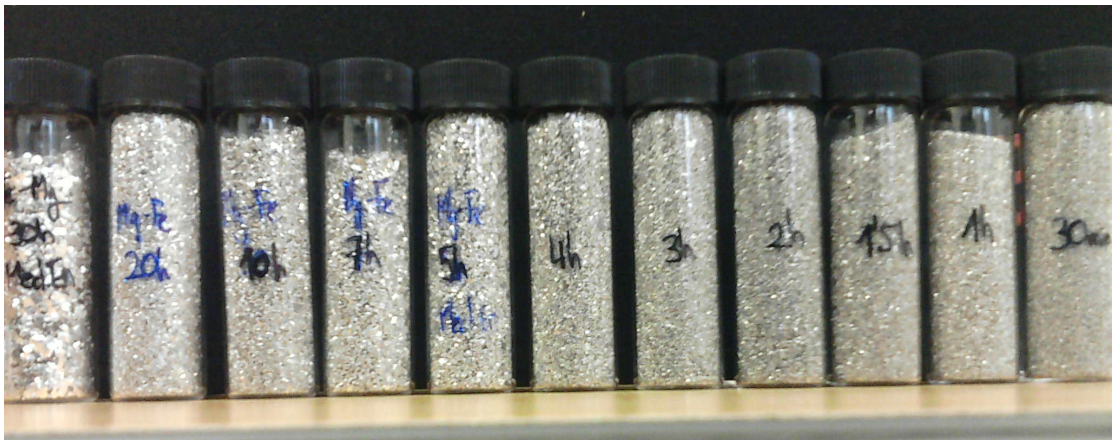


Figure 23 All MEBM powders

- Temperature of Milling: The temperature was not controlled. In every sample fabricated, the temperature was free for variation.

4.4. PROCEDURE

Once all the variables were set, and the equipment ready, the experimental process could take place. The procedure was always the same, no matter if it was for the LEBM or the MEBM.

Firstly, the LEBM powders were made. Making sure all the appropriate conditions were set, the powders were weighted in their arranged proportion, and so were the balls (grinding medium). Once the powder and the balls were poured in the milling container, this one was introduced in the vacuum chamber, with its open lid, in order to create an Argon atmosphere. Inside the chamber it was closed air-tightly, so that it was sealed from the exterior atmosphere. Now it was possible to introduce the milling container with its interior filled, into the energy ball mill selected, setting the time and speed.

When the MA powders had been made with the LEBM, and later with the MEBM, it was time to observe the powder through the magnification lenses of a microscope. The surfaces of all metallographic samples were prepared by various methods of polishing, and etching. After preparation, it was always analysed using optical or electron microscopy.

4.4.1 SAMPLE PREPARATION

Before been able to observe the microstructure through the microscope, all samples should be prepared for this purpose. Mechanical preparation is the most common preparation method. In a series of steps, successively finer abrasive particles are used to remove material from the sample surface until the desired surface quality is achieved.

- Mounting:

The first step is to prepare the mounted sample for every MA powder. Throughout the whole research, the process followed was the same. The MA powders were placed in their mounting cups, and a mounting material was then pored over. The AMPL used as mounting material a mix 25:3 in weight of Epoxi Resin and Epoxi Hardener, both from *Struers*. After pouring the mounting material, it was left for 6 hours to harden.

Figure 24 During one sample mounting

- Grinding and polishing:

With the mounted sample prepared, the second step of preparation would be, grinding. The purpose of grinding and polishing is to produce a suitable surface by means of a step-by-step removal of deformed material until it becomes negligible. The polishing was first conducted using manual technique on fixed abrasive sand papers, starting with 800 (CC261) until the sample was flat, and followed by successive papers of finer abrasivity, to end in the polishing machine with alumina slurry on microcloth.

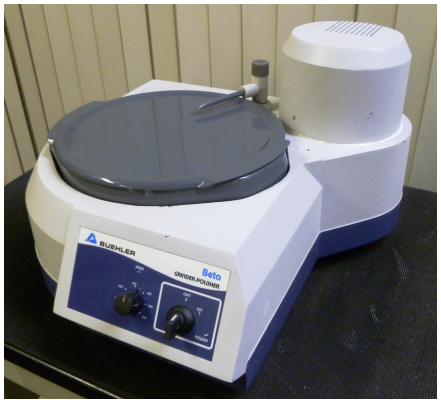


Figure 25 Polishing machine: Buehler Beta

The AMPL provided a Buehler Beta Grinder-Polisher machine. Although certain information may be obtained from as-polished specimens, the microstructure is usually visible after etching. Only in microstructures, which exhibit strong colour features differences, can be viewed without etching. The study case, due to the different colour of the constituent's materials, it was possible to determine certain amount of clarity without etching.

- Etching:

Using a suitable chemical etchant it was possible to reveal clearly the microstructural constituents of the specimen (grains, defect, etc.). A great many etchants have been developed to reveal the structure of metals and alloys, ceramics, carbides, nitrides, and so forth. For the etching of all samples the

chemical etchant prepared was a mixture of Nitric Acid (1-8ml) and Ethanol (100ml) leaving the specimen in the etching solution for 12secs [19].

Only in the cases where the OM showed at least a minimal indication that the MA could be working in the desired direction, it would be decided to make more investigation using the XRD, and the SEM. If through the observation of the OM it was possible to see that some Fe particles were covering the Mg then it would be worth to investigate more profoundly with the electronic equipment available.

- XRD Preparation:

In a typical XRD experiment, a thin layer of crystalline powder is spread onto a planar substrate, which is often a non-diffracting material such as a glass microscope slide, and exposed to the x-ray beam. The quantity of powder used for each experiment is quite small, typically on the order of a few milligrams. Ideally, the specimen should contain a large number of small, equiaxed, and randomly oriented grains.

- SEM Preparation:

Specimens for observation in the SEM do not need to be extensively prepared; they do not need to have a mirror-like surface finish like required for the OM examination. However, to obtain good images, it is necessary that the specimen:

- Contamination free surface
- Is stable under vacuum system and under electron beam
- Does not build up an electrostatic charge on the surface

The non-conducting specimen surface will be coated with a thin layer of an electrically conducting film; in this case, a thin layer of carbon is deposited for this purpose with an EMITECH K575X Sputter-Coater as shown in Figure 26.

Figure 26 EMITECH K575X Sputter-Coater

And for the same purpose, the specimens will have conducting tape attaching the sample to the specimen holder.

5. RESULTS AND DISCUSSION

Through the observation of the different powders microstructure, with destructive and non-destructive testing, it was possible to determine certain hypothesis. But only using specialized equipment, as SEM and XRD, it was possible to reach final conclusions. The first experiment held was the LEBM, obtaining three powders.

5.1. LOW ENERGY BALL MILLING

The firs attempt would be with LEBM. Three samples were made, one for 30min of MA, another for 10 hours, and a last powder for 30 hours of MA. All of these samples were polished and observed through the OM. On Figure 27 it is possible to appreciate the microstructure for the 30 minutes MA powder.

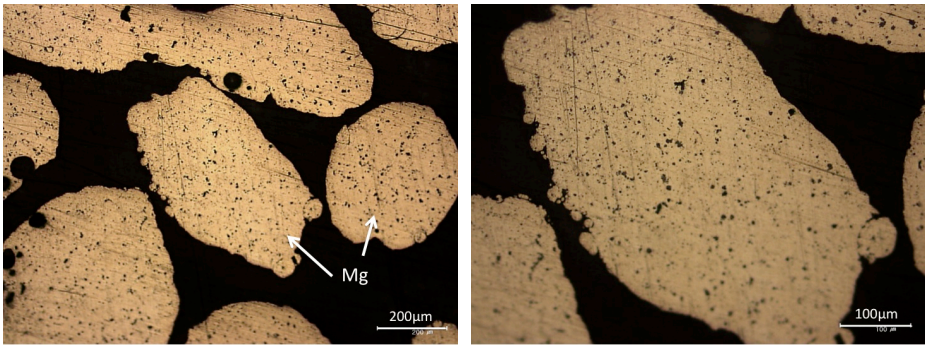


Figure 27 Micrographs low and high magnification for 30min MA powder with LEBM

As the micrographs on Figure 27 display, the Fe has not begun to gather around Mg particles. Therefore, it was decided to change one of the process variables. As explained previously, the variable that would be varying was the milling time. Therefore, on Figure 28 we have the micrograph for 10 hours of milling time in the LEBM.

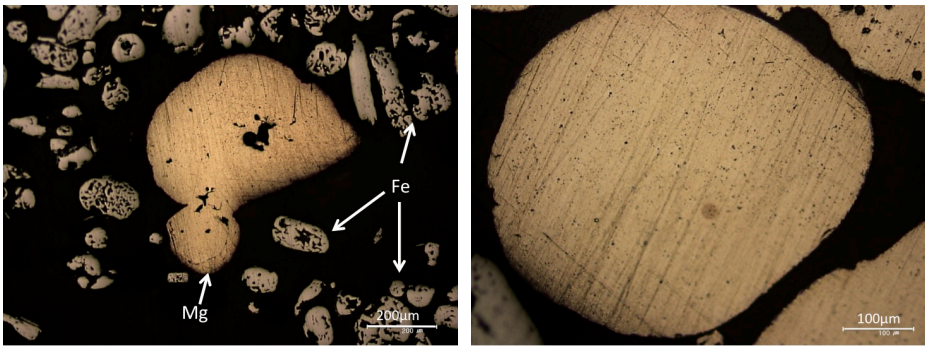


Figure 28 Micrographs low and high magnification for 10hours MA powder with LEBM

Still it is not possible to appreciate a significant amount of Fe surrounding any of the Mg particles. Neither it is possible to suggest that the Mg particles are

increasing in size due to its ductility. Once more, the milling time is increased, this time up to 30 hours of milling time, representing the micrographs on Figure 29.

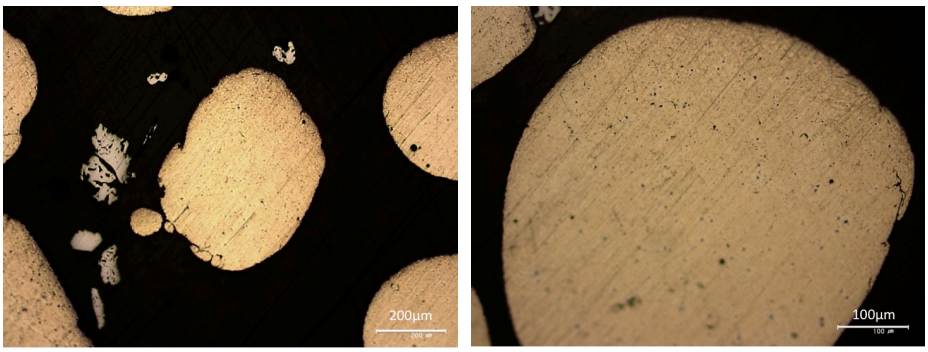


Figure 29 Micrographs low and high magnification for 30 hours MA powder with LEBM

Again, after a close look with the OM, with high magnification up to 200X, the micrographs do not show any signal that can prove this MA to be welding together the elements. Looking closely to the grain borders of the Mg particles for the 30 min, 10 hours, and 30 hours samples, it is not possible to distinguish the susceptible Fe attached.

Just in case, knowing that there is a chance that the Fe cover surrounding the Mg is so thin that can not be seen with naked eye, or the possibility that it was removed during the polishing, it was decided to etch all samples, and observe the microstructure for any other sign on this level. All samples were etched with the same solution and the same amount of time.

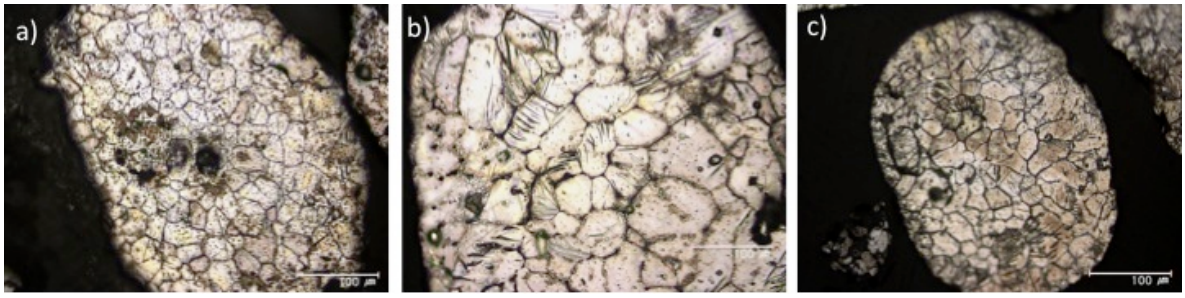


Figure 30 High magnification micrographs after etching of LEBM samples for a) 30min, b) 10 hours, and c) 30 hours of milling.

Corroborating the initial hypothesis, the cold welding characteristic of MA has not been sufficient for attaching an Fe coat around the Mg as the research is focusing in. Several images were taken from the OM, and as it reflected on Figure 30, with a high magnification micrograph for each specimen, and no track of iron was found over the edges. There must be a problem with the process variables elected, because MA has characteristically been a major cause of cold welding and fracturing, another thing that cannot be identified in the analysis of the various micrographs.

Therefore, it is necessary to make some changes to the initial experimental process variables. This is the reason why in the next study, the MA

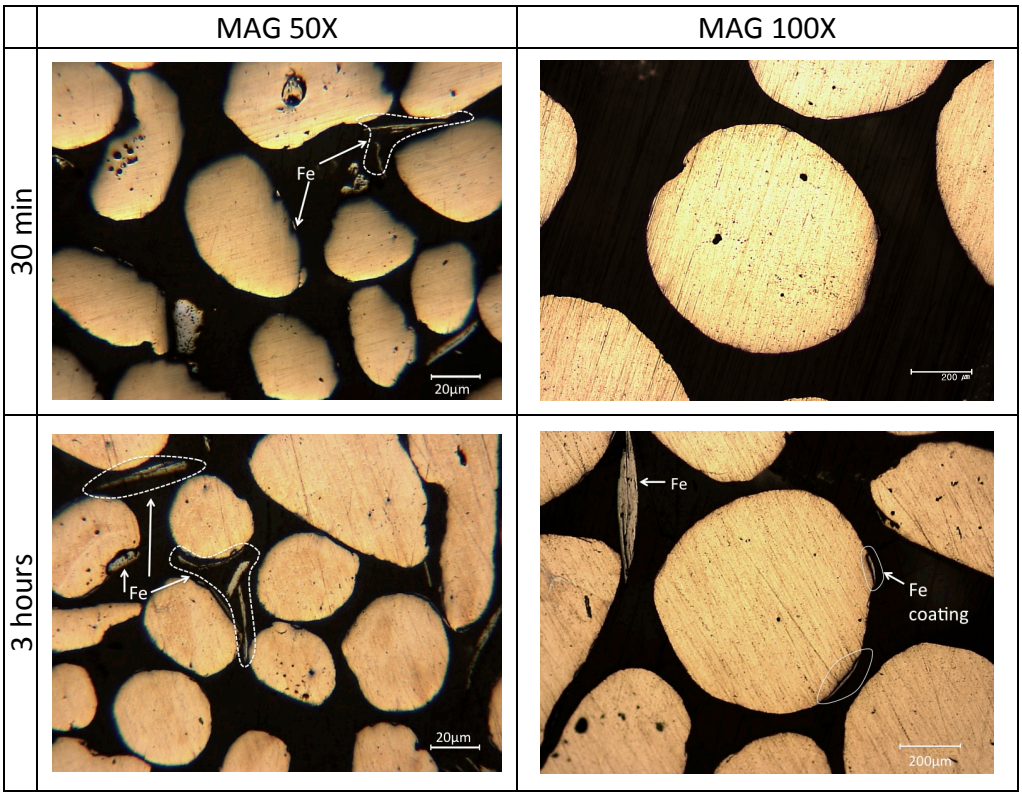
will be held on a MEBM, and, in order to transfer more power into the powder particles, the milling speed and the size of the grinding medium will be increased.

5.2. MEDIUM ENERGY BALL MILLING

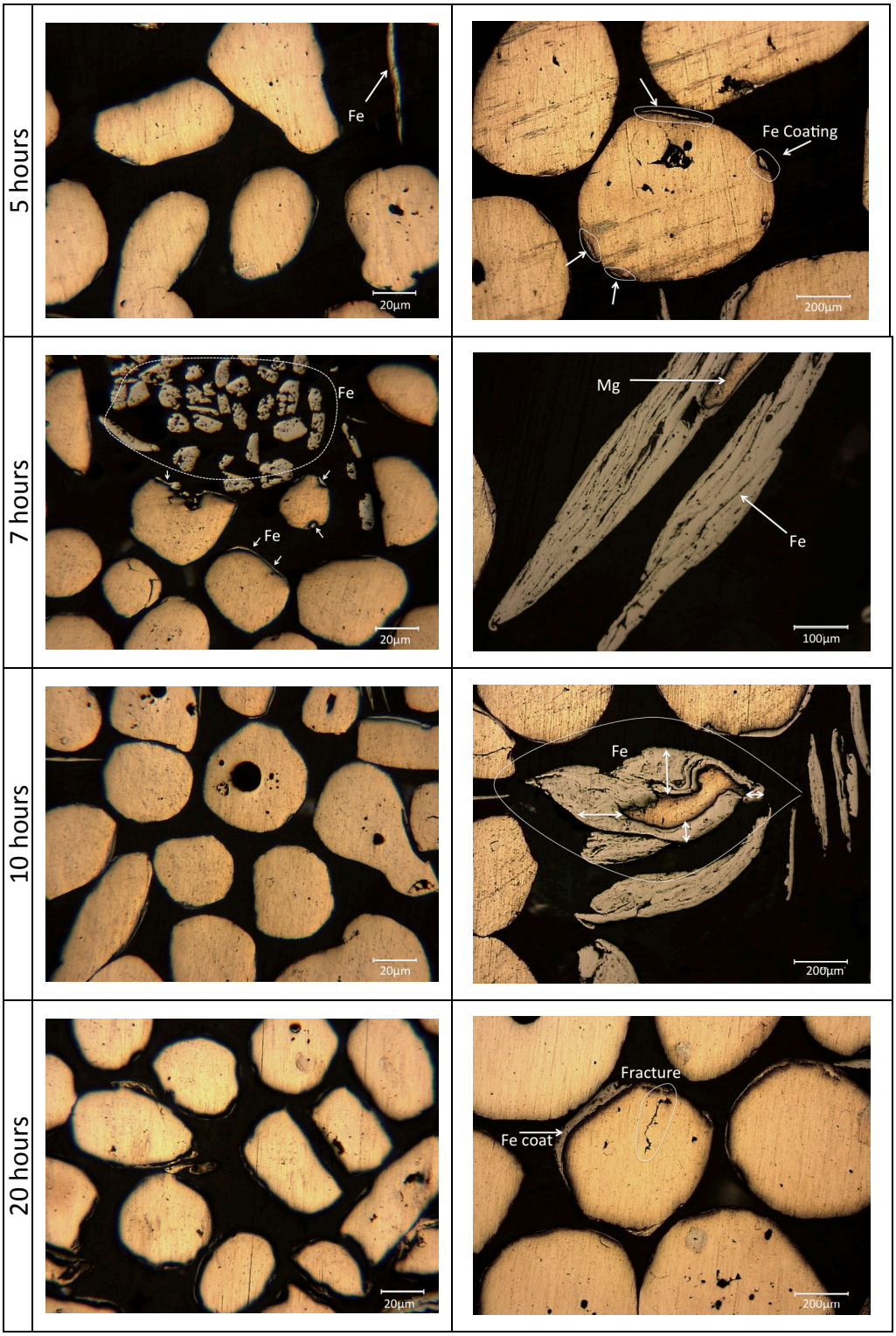
On this part of the research, more MA powder samples were made[1]. As the experimental process took place, the researchers found out new evidence that encouraged making more powders, from the three initial samples, up to twelve different MA powders, narrowing the experimental conditions to obtain the proper coating searched for, by increasing the milling time. As it will be demonstrated, the milling time also has its limits, and if excessive milling is done, the powder is ruined.

5.2.1. OPTICAL MICROGRAPHS

Once the samples were mounted, grinded, and polished appropriately, they were taken into the optical microscope.



[1] Based on the arranged conditions explained throughout the experimental process, the MEBM was conducted with a few alterations of the initial conditions


5 hours
Fe
20µm
Fe Coating
200µm
7 hours
Fe
Fe
20µm
Mg
Fe
100µm
10 hours
20µm
Fe
200µm
20 hours
20µm
Fracture
Fe coat
200µm

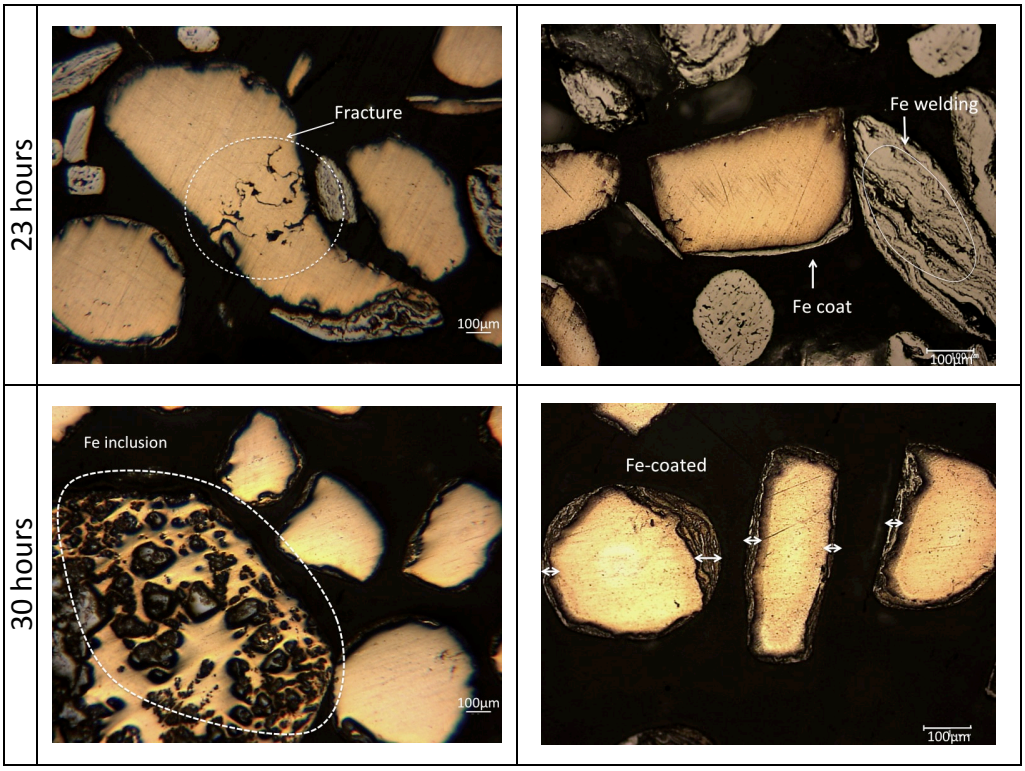


Figure 31 Optical micrographs of different milled powders with MEBM

The various micrographs exhibited on Figure 31 show the state of powder after milling for the different milling times, in low and high magnification. It is possible to obtain certain information observing these images.

At first glance, one can have a general idea of the process that has undertaken; it looks as if some Mg particles grow with the milling time, and later fracture, thus cold welding and fracturing is a frequent process during MA. At 20 and 23 hours after milling, it has been highlighted on the micrographs how particles are breaking through fractures. Also, after 30 hours of milling it is possible to appreciate in the micrographs, how some particles have been spoiled, whereas others are in perfect coating condition. Excessive milling time turns our particles into an undesirable intermetallic.

What really is interesting in this study is that from the OM images, it is possible to observe that an Fe coating has taken place. In order to determinate, it is necessary to observe higher magnification micrographs shown on Figure 32.

From the micrographs exposed on Figure 32, it is clear that the research is on the right track to satisfying the initial goal. In the first stages, where the powder was milled 30min, 1hour, 2 hours, 3 hours… up to 5 hours, the Fe coating seem to be growing in thickness and quantity, but not enough for its final purpose (the arrows indicate on Figure 32 the position of the coating). The amount of Fe coat could be approximately of 50% after 5 hours of milling. By increasing milling time it was possible to increase the surface coat, to approximately 80% on average at 20 and 23 hours of milling.

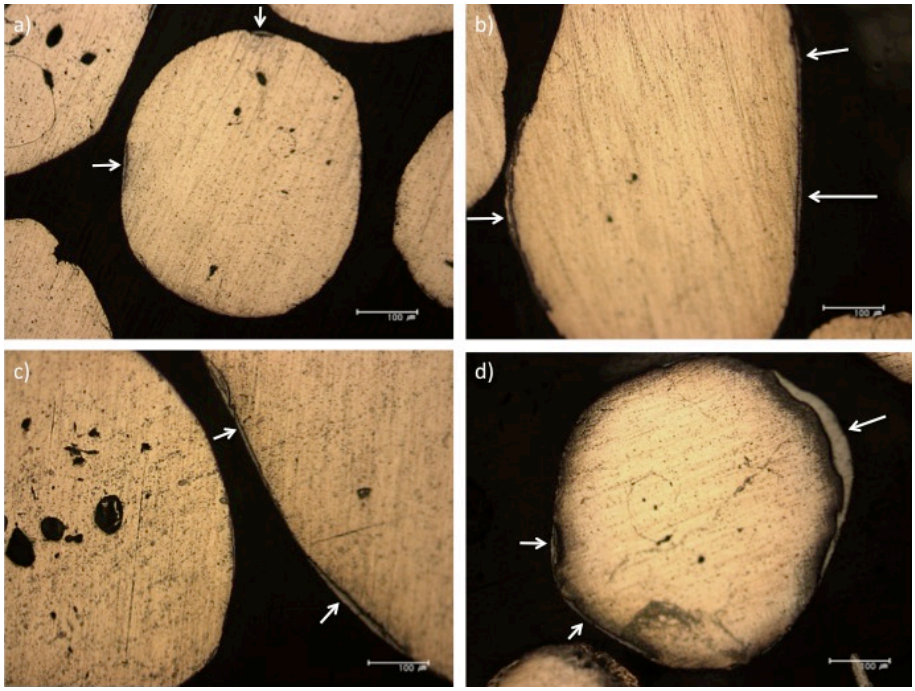


Figure 32 High Magnification micrographs of MEBM for a) 1 hour, b) 5 hours, c) 10 hours and d) 20 hours

These are only approximations based on the micrographs observed, further investigations measuring the coat thickness (with the program SemAfore 5.21) of the micrograph, show that the on average, the thickness is really increasing with time.

Hours Milled	Average Coat thickness (µm)
1	3,8
3	4,2
5	6,3
7	5,2
10	11,6
20	13,1
23	11,2
30	15,1

Table 3 average coating thicknesses with milling time

Results on Table 3 are encouraging; knowing that increasing the milling time, and having changed the grinding balls size, is actually making a difference. It will necessary to determine the coating composition.

It is noteworthy to take notice of the Fe particles. In the first stages of milling, it is possible to appreciate how the Fe particles are first sharpened and enlarged in an arrow like shape.

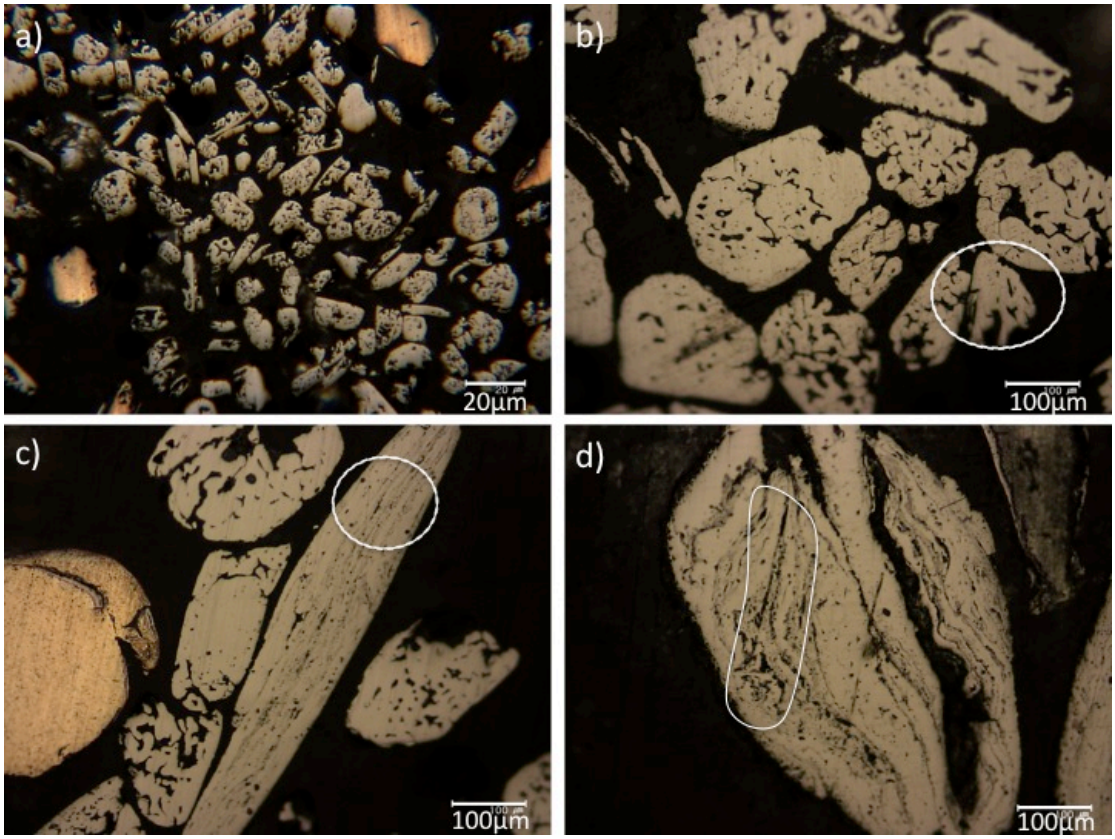


Figure 33 High magnification micrographs of Iron evolution for a) 5hours, b) 7hours, c) 10 hours and d) 20hours

But the longer the milling process extends, the bigger the Fe particles become, sticking one to another. On image a) most particles are still small, but after 7hours, on b), most of them are bigger than the marked particle. So it reasonable to think that the MA is making the iron particles sharpened (flakes are formed due to the ductility of particles), and then through cold welding growing in size (see Figure 33 c; it is possible to observe how big particles of Fe are made of more than one particle of Fe, the borders are still visible in image d).

Although not all the powder behave in the same way, visibly there is a common movement where Fe particles grow in size unifying with milling time, whereas Mg particles grow at first stages and then fracture, through the whole process some Fe particles coat the Mg, but unfortunately Fe particles are still free from Mg even after 30 hours of milling.

However, it is necessary to prove this hypothesis through other analytical means, in order to establish a firm conclusion. It is advisable to observe the milled powder for more information about size and coating experience.

5.2.2. SEM MICROGRAPHS OF MILLED POWDERS

The SEM was used to study changes in shape, size and coating of the milled powder during different stages of the milling process. The Figure 34 shows the SEM images of pure Fe and pure Mg used to make the powder at different magnifications.

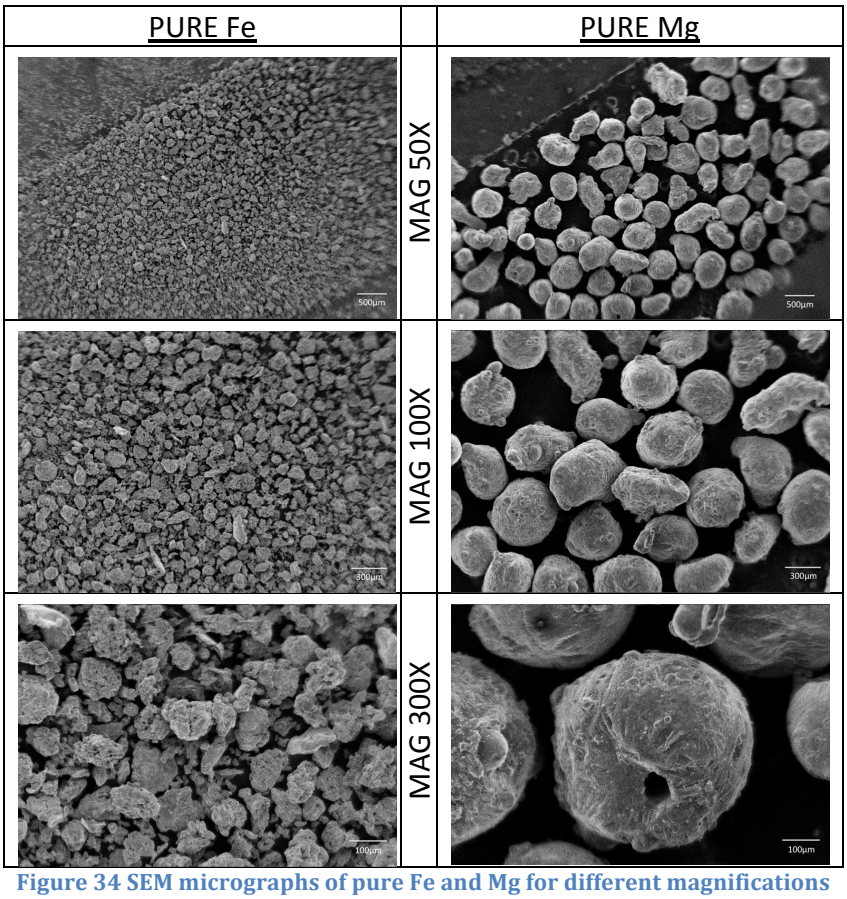


Figure 34 SEM micrographs of pure Fe and Mg for different magnifications

The original powders size were 180µm for Fe, and 700µm for Mg particles. Relying on the original powders, it facilitates the operation of identifying the geometrical changes of the different milled powders. Out of these micrographs one should have a general idea of the shape, surface and size of the particles.

The following Figure 35 has on display micrographs for a number of different milling times and magnifications.

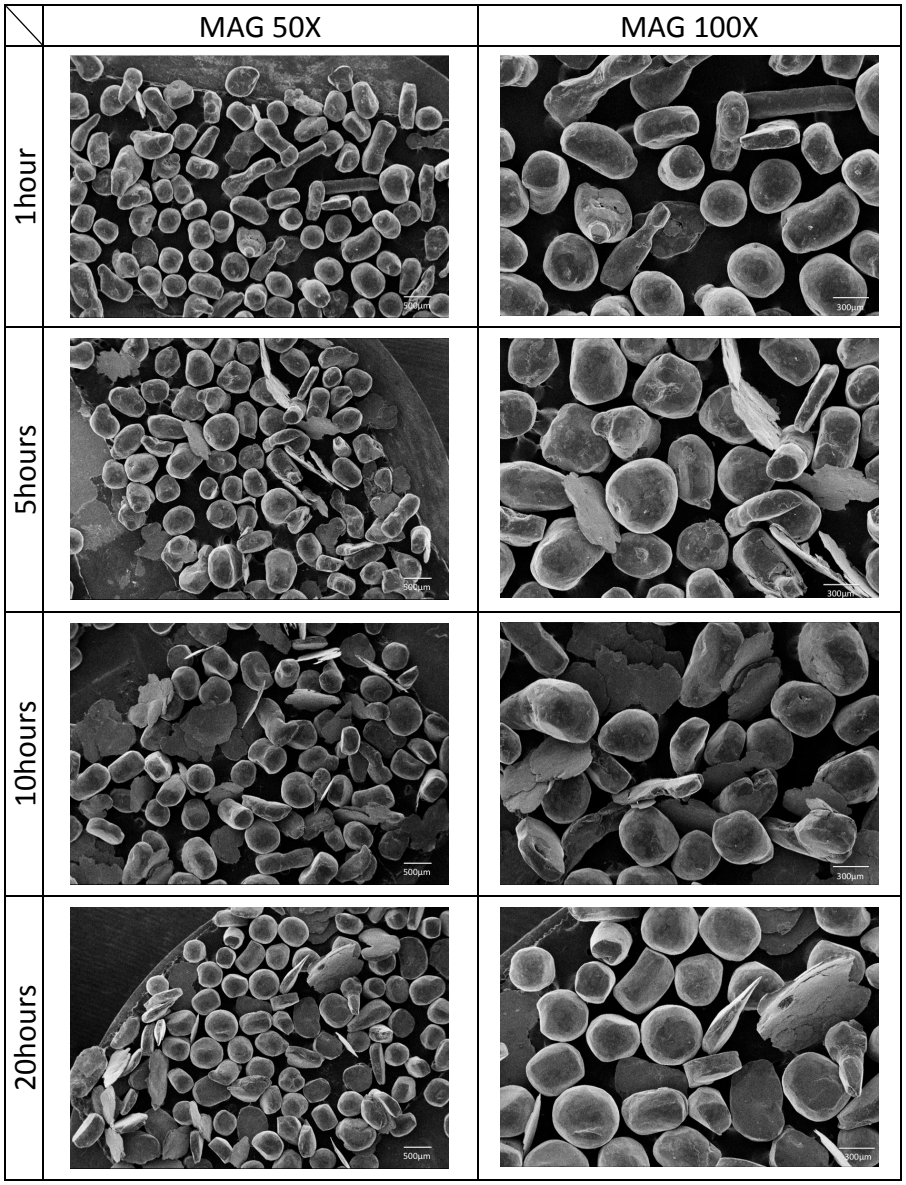


Figure 35 MEBM micrographs of milled powder for different milling time and magnification

The reader can appreciate on Figure 35 how from 5 hours on, there are several particles that seem flattened. Mg is fairly ductile, and the high energy acquired during the MA has plastically deformed some particles. As we increment the milling time, the number of particles plastically deformed also increases. More and more particles seem to be flattening. This is a problem, which should be maintained under control in case of reaching high percentages of the total powder.

Another aspect to be taken into consideration should be the particle size. It is characteristic of MA and of the refinement process that particles grow in size at first stages, for a later brake into smaller pieces, due to cold-welding, fracturing and re-welding. However, although it is difficult to appreciate, comparing in magnification 100, from 1hour to 5 hours there is a real difference in size.

The SEM provides a clear and closer image of certain particles augmenting magnification. It is interesting to zoom in a certain particle to analysis its surface. The object of study is an Fe-coated surface of Mg, and on Figure 36 it is possible to examine the particles surface for a number of different milled powders[2].

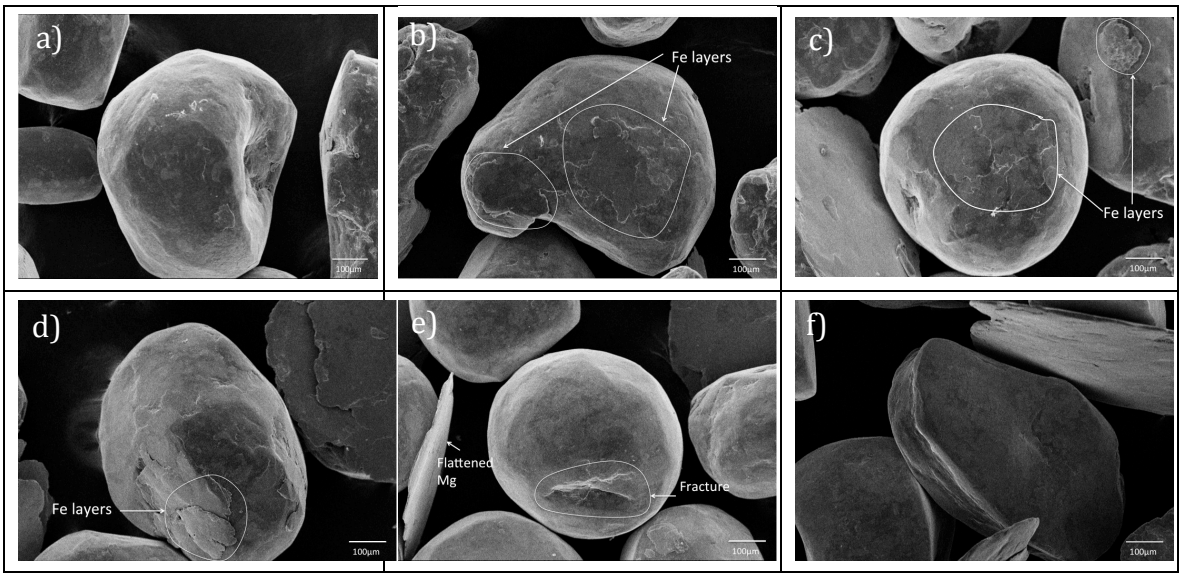


Figure 36 SEM micrographs for MEBM powders with high magnification; a)1hour, b)3hours, c)5hours, d)10hours, e)20hours and f)23hours

Comparing the initial pure powder images on Figure 34 with the ones on Figure 36 above, the surface of the magnesium particles has smoothen, and in some cases, added material. On the pure magnesium particles it is possible to see the rough surface, with picks and lumps, where in the other hand, on the milled powders the surface is more regular, with some irregular surface highlands. Taking a closer look at images b) c) and d), it is marked where the surface has pieces of Fe stuck to the magnesium surface.

Once again, analysing the SEM micrographs, one can observe how some flatten particles are appearing with longer milling times. Its percentage with the total powder is significant, but not disturbing. After 23 hours, the flatten particles reach approximately 20% of the total powder sample.

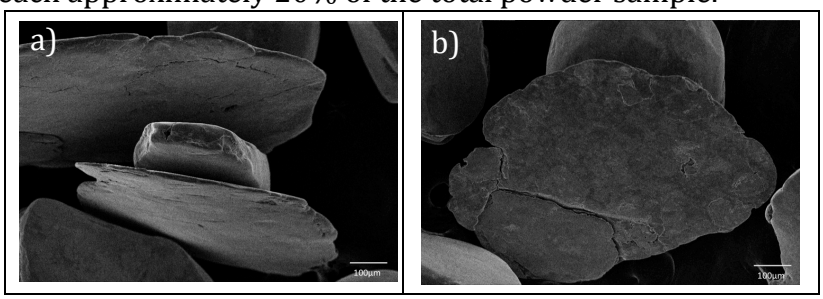


Figure 37 SEM micrographs for 23 hours milled powder on MEBM

[2] Again, some of the MA powders do not add any additional information and will not be displayed.

Because the variation of particle size is hard to see with the naked eye, in order to explain how it has been varying with time, a tedious work of particle measurement was realized.

5.2.3. PARTICLE SIZE DISTRIBUTION OF MILLED POWDER

In order to measure the particle size, several micrographs were meticulous studied through the SEMAFORE 521 program. Previous to analysing the results, a necessary remark should me mentioned; Mg and Fe powder were measured with the same technique, and the average particle size resulted in 450µm in Mg and 110µm in Fe, differing from the original powder stipulations (700µm, 180µm respectively).

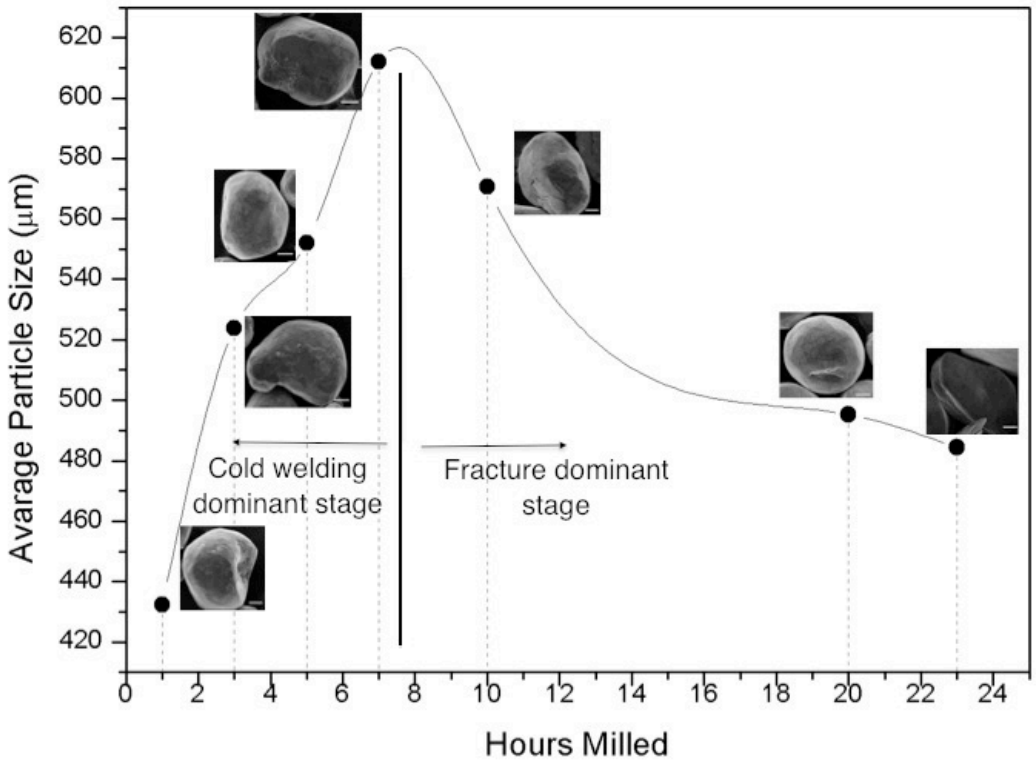


Figure 38 average particle size distributions with time (picture scale 100µm)

With the measuring computer program and a selection of milled powder micrographs (1 hour, 3 hours, 5 hours, 7 hours, 10 hours, 20 hours, and 23 hours -Figure 35), ten measures were taken from each image. Calculating the average size for each milling time, and scheming the results on Figure 38.

As it had been guessed from the OM and SEM micrographs, the particle size truly changes with the milling time. The MA powder after 1 hour of milling has an average size (430µm) under the original Mg size. Continuous milling produces successive cold welding, making the particles grow bigger. This stage where cold welding is the dominant activity continues to 8 hours of milling (where it reaches 620µm). If the milling is continued in time, the graph shows a

new stage where fracture is the dominant activity, cracking into smaller pieces the particles (see Figure 36 e, Figure 31 in 20 an 23hours). Subsequently it is clear that by changing the milling time, the powder experiences size change. Results of Figure 38 expose a typical ductile material reaction with milling time. Ductile materials behave characteristically forming a mountain kind of shape, but brittle materials behave in a complete different way with milling time. A brittle material like Si is likely to have a particle refining performance with milling time, as exposed on Figure 39.

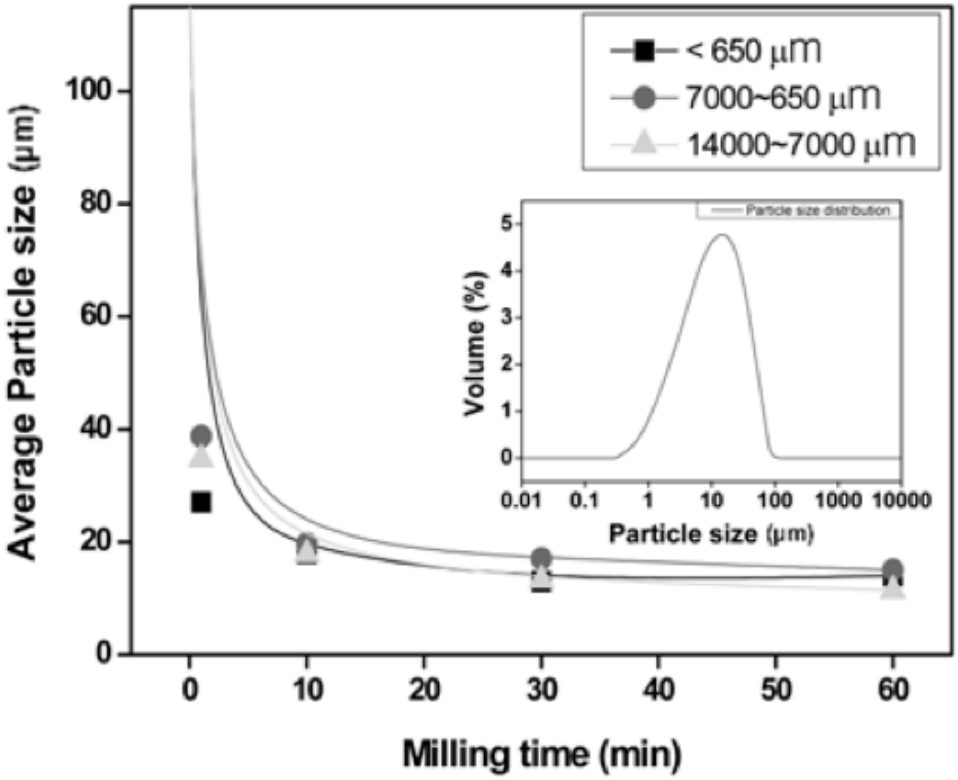


Figure 39 Particle size distribution of Si

Evidently, the powder's size behaviour with time is proper of ductile materials (raw materials; Fe and Mg). The present study research is focused on adding material to Mg particles (Fe coat) and not on particle refinement. Therefore results correspond with what it was estimated, that after 23 hours of milling the particle size would be slightly bigger than the initial, due to a Fe coating.

5.2.4. XRD RESULTS WITH MILLING TIME

Every remarkable Fe coated Mg powders were studied by an XRD pattern, using a Cu Kα radiation (λ=0,15406nm), obtaining the patterns exhibited on Figure 40. The horizontal axis records angles in degrees (2Theta), and the vertical axis records X-ray intensity.

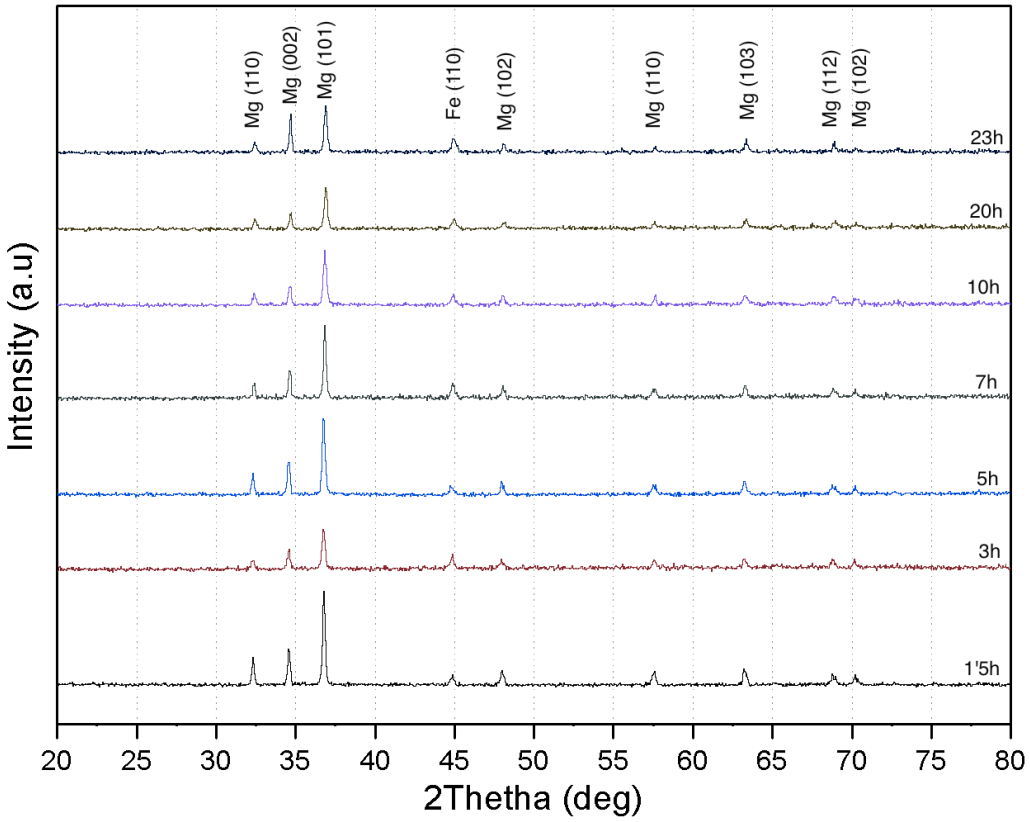


Figure 40 X-Ray traces of Fe coated Mg powders with milling time

As it is showed on Figure 40, every peak has been assigned its correct Miller indices. The lattice parameters have been assigned according to the ICDD[3]. On the pattern the highest intensity peak for Fe is located in the original angle, at approximately 45deg, as the Fe has a BCC (highly symmetrical) structure, it is expected that the number of peaks is low, on the other hand, Mg has an HCP (poorly symmetrical) structure, which increases the number of peaks. Likewise, Mg highest peak at lattice (101) is represented in the original angle – (36deg). Mg higher peaks are well represented through all the milling times. Therefore, every peak belongs to one of the studied materials; it is irrefutable that Mg and Fe are two different compounds.

At the 1'5 hour pattern, it is appreciable that the intensity on Mg higher peaks is much bigger than Fe; this is due to the difference on material quantity at the original mix, where we made a 7 to 3 material relation. As the milling time is increased, the intensity differential of the peaks decreased. That symptom reflects the continuous appearance of a growing Fe coat (which increases with the milling time), due to the creation of bonds between Fe-Mg particles.

Therefore the XRD traces of Fe coated Mg powders for various milling times, indicate the non formation of new reaction phases with the milling, only represents the input elements of Fe and Mg.

[3] For further information in the appendix are Mg and Fe Diffraction Data from ICDD.

5.2.5. ENERGY-DISPERSIVE X-RAY SPECTROSCOPY RESULTS

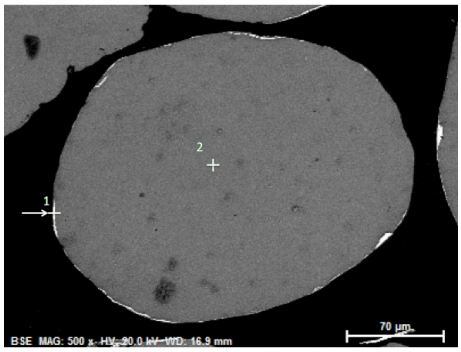
EDS is used as an analytical technique for chemical characterization of the samples. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure; in this case Fe has BCC and Mg, HCP, allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely.

Unfortunately the accuracy of EDS spectrum can be affected by many factors. It is very common that elements from the carbonized layer of the specimen or from the rapid oxidation of Mg appear on the spectrum. On the following data obtained, the non-significant elements where removed, and the percentage's rearranged, although the graphs could not be readjusted and show some of the irrelevant elements (C, O).

In the resulting cross-sectional micrographs taken by BSE (often used in analytical SEM along with the spectra made from the characteristic X-rays), there are two spectrums that are analysed. All pictures have the same order; spectrum 1 is chosen inside the coat, and spectrum 2 in the inside particle.

Judging the micrograph on Figure 41, after 3 hours of milling the coated surface is not even covering 50percent of the whole particle's surface (on the BSE micrographs, the white matter is the coating). By analysing the composition in the spectrums, it is clear that the inner part is just Mg, no mixture. But, when we analyse the coating (spect1), we realize that it is a mixture of Mg and Fe, and even more surprising, that Mg is the abundant compound.

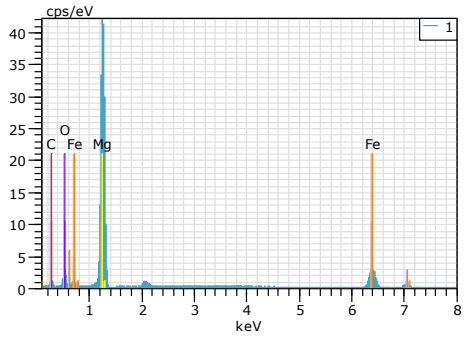
After the XRD study, it is clear that there are no intermetallic compounds created by the milling, so this behaviour is due to two main reason; firstly, the coating layer is too thin, and secondly, as we show on OM, in many cases the coating is made up of layers of flattened particles Mg-Fe indistinctively.

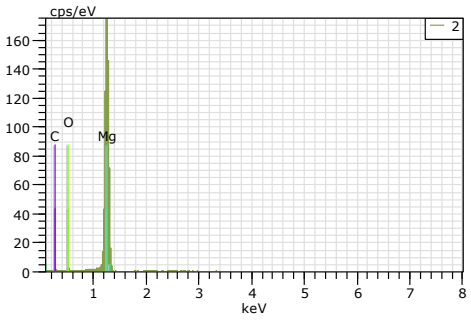


3 Hour

Spectrum 1		
Element	wt. %	at. %
Magnesium	77,12	88,56
Iron	22,88	11,44

Spectrum 2		
Element	wt. %	at. %
Magnesium	100	100

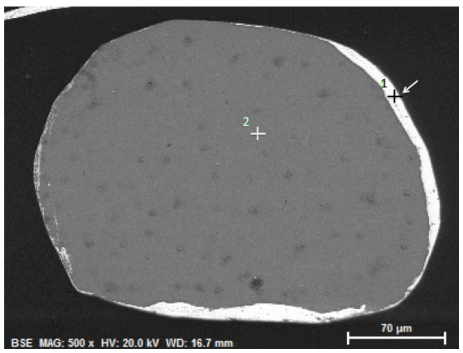




SPECTRUM 1 SPECTRUM 2

Figure 41 EDS for 3 hours milling

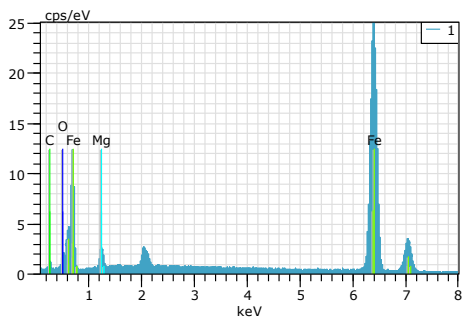
Therefore, it is logical that as the coating layer gets thicker, those reason do not affect as much, and the coated composition adjusts better our expectations. The inner spectrum2 is still Mg after 10hours (see on Figure 42), and the coating, spectrum1, is mainly constituted of Fe. Up to 94,47% of atoms are from Fe.

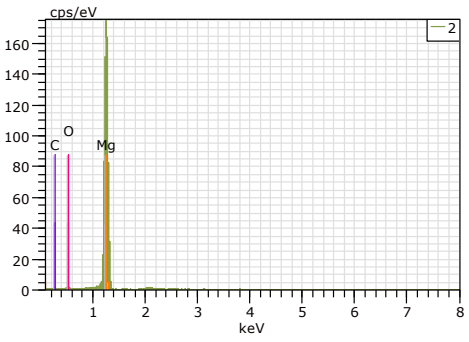


10 Hour

Spectrum 1		
Element	wt. %	at. %
Iron	97,5	94,47
Magnesium	2,5	5,53

Spectrum 2		
Element	wt. %	at. %
Magnesium	100	100

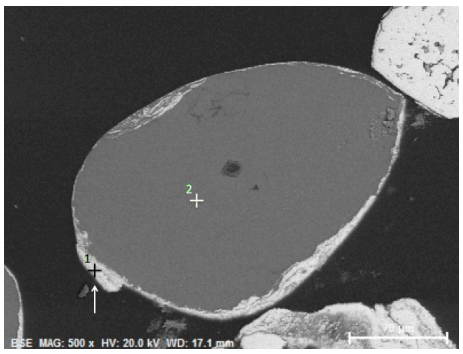




SPECTRUM 1 SPECTRUM 2

Figure 42 EDS for 10 hours milling

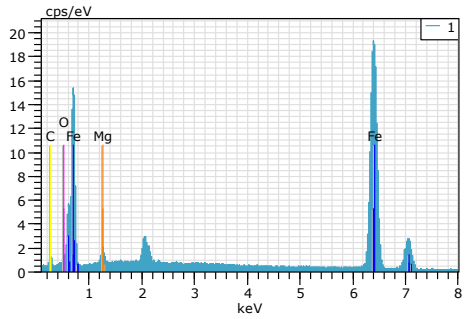
If the milling process continues, up to 23 hours (observe Figure 43), the surface coated reaches 100% of the particle, although not homogenous, the element composition is near the optimal. The spectrum of in the coat (spect2) is almost free of magnesium.

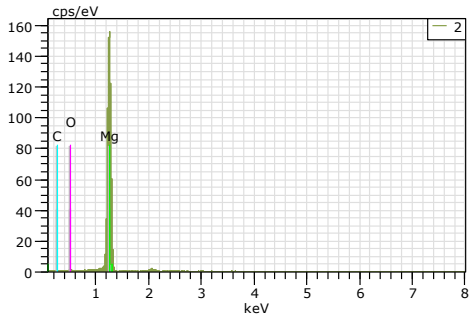


23 Hour

Spectrum 1		
Element	wt. %	at. %
Iron	99,76	99,44
Magnesium	0,24	0,56

Spectrum 2		
Element	wt. %	at. %
Magnesium	100	100





SPECTRUM 1 SPECTRUM 2

Figure 43 EDS for 23hours milling

Considering the factors that contaminate the specimen composition, it is believed that milling longer time benefits the purpose of reaching a steady and fully Fe coat of the Mg particle, and additionally the coated layer gains Fe pureness.

6. CONCLUSIONS

Afterward the creation of a number of powders, through mechanical alloying technique, for a variety of different milling times and after exploring with a diversity of energy ball mills, regarding the promising results and their discussion on the present study, the conclusions obtained are as exposed.

- The production of Fe coated particles of Mg cannot be achieved through low energy ball milling, with zirconium 2mm balls, independently of the time milled.
- Augmenting speed and grinding balls; using a medium energy ball milling with 600rpm and steel balls of 3,2mm, MA techniques are capable of developing an iron coat over magnesium particles.
- Improvements in the coating process can be achieved through an augmentation of the milling time. By increasing the milling time to a maximum of 23 hours:
    - The surface of Fe coat increases, and ultimately surrounds the whole particle.
    - The thickness of the coat broadens and reaches successfully 15μm.
    - The Mg particle size undertakes a series of variations; with short milling times rises to a maximum of 620μm, and with longer times up to 23hours, decreases to 480μm.
    - The Fe particles join together forming big conglomerates.
    - Composition of the coating layer improves its iron purity.
- Excessive time is responsible of undesirable effects. When milling time exceeds 23 hours:
    - The magnesium ductile particles suffer an extreme deformation, ruining the powder.
    - Results in formation on intermetallic compounds.

Therefore, for future studies on sulphur removal of the iron melt, experimental analysis indicates that the optimal coated powders are created after 23 hours of milling.

Initial requirements to support the severe conditions inside the iron melt are accomplished by mechanical alloying; with MEBM and a speed of 600rpm. On Figure 44 a final brief process is exhibited.

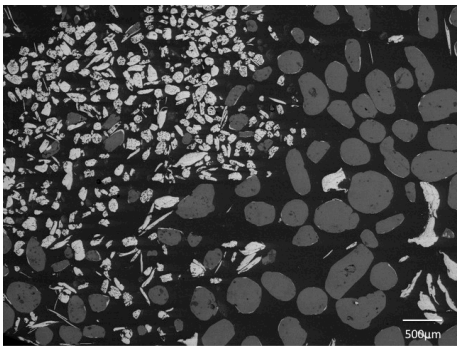
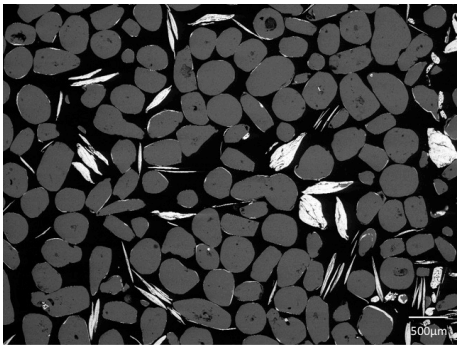
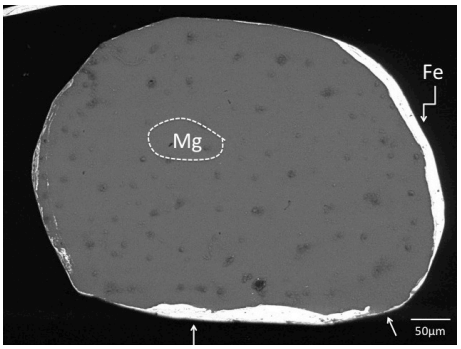
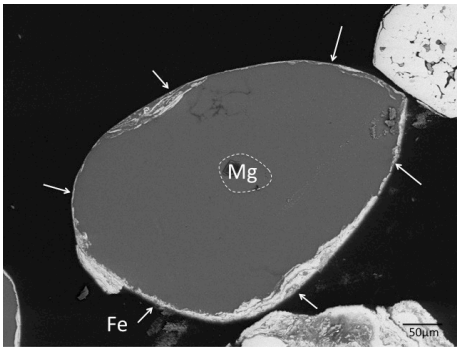
MILLING TIME	MICROGRAPH	RESUME
3hours		Fe non-homogenously distributed. Mainly spherical particles. (Fe white particles)
5hours		Fe homogenously distributed. Arrow shaped. (Fe white particles)
10hours		Coating surface is significant.
23 hours		The coating is complete.

Figure 44 Coating process steps

7. FUTURE

It becomes amply clear that the technique of MA is very efficient in synthesizing a variety of equilibrium and non-equilibrium materials. Some of the present issues that need immediate attention are that we need homogeneous, pure, macro-defect (i.e., porosity and cracks)-free and fully dense materials for obtaining reproducible results. Further, larger-scale applications require materials that could be produced in tonnage quantities, and materials that have been well characterized and exhibit reproducible properties and also exploit them for commercial applications. But, the bane of MA has been the three C's – Cost, Consolidation, and Contamination. Powder processing is expensive and therefore, unless one is able to identify niche markets for the MA products and the powders produced in large volumes, cost is likely to continue to be high.

However, in some cases, e.g., hydrogen storage materials or magnetic alloys, the high cost may be acceptable in view of the improved properties and enhanced performance. Consolidation of the milled powder continues to be a serious problem. There have not been many investigations to report successful consolidation of MA powders to achieve full density and simultaneously retain the metastable effects.

Newer and improved methods of modification/combination of the existing methods may be necessary [15,16]. The last point is that contamination of the MA powder has been a serious issue in many cases [5]. Some solutions have also been suggested to minimize/avoid contamination completely. These include enclosing the mills inside chambers that have been evacuated and/or filled with an inert gas, or using high-purity gaseous atmosphere in which the powders could be milled. Both options could be expensive and/or impractical.

The MA powders could also be used in the asproduced powder condition without consolidation. Examples for such applications include use as catalysts, pigments, solder, hydrogen storage materials, etc. In that case, some of the above problems may not be relevant. Further, even if a bulk component made of MA powder needs to be used, if that material could tolerate high gaseous impurities, then also there is no problem. But, with the intense research activity going on all over the world, there is great potential for MA products and bright future for research in this area [11].

BIBLIOGRAPHY

- **Cast irons** By Joseph R. Davis, ASM International. Handbook Committee
- **Degarmo's Materials and Processes in Manufacturing** By E. Paul DeGarmo, J. T. Black, Ronald A. Kohser
- **Materials science and engineering: an introduction** by William D.Callister
- **Mechanical Alloying and Milling** by C. Suryanarayana
- **Experimental Techniques in Materials and Mechanics** by C. Suryanarayana
- **Mechanical Alloying.** Ed. P. H. Shingu. Trans Tech Publications (1992).
- **The history of grinding** By Alban J. Lynch, Chester A. Rowland.
- **Mechanical alloying** by Li Lü,Man On Lai.
- **Mechanical Alloying: Fundamentals and Applications** by P. R. Soni
- **Structure and Properties of Engineering Alloys** by Smith, McGraw Hill
- www.icdd.com/
- **X-Ray diffraction: a practical approach** By C. Suryanarayana, M. Grant Norton

LIST OF FIGURES

LIST OF TABLES

REFERENCES

1. **Materials science and engineering: an introduction** by William D.Callister
2. **Cast irons** By Joseph R. Davis, ASM International. Handbook Committee
3. **http://www.mineralszone.com/minerals/iron-ore**
4. **Degarmo's Materials and Processes in Manufacturing** By E. Paul DeGarmo, J. T. Black, Ronald A. Kohser
5. **Mechanical Alloying and Milling** by C. Suryanarayana
6. **The history of grinding** By Alban J. Lynch, Chester A. Rowland
7. **Practical ODS Alloys, Materials Science and Engineering**, H. K. D. H. Bhadeshia,
8. **Progress in Materials Science** 46 (2001) 1-184 by C.Suryanarayana.
9. **Mechanical alloying** by Li Lü,Man On Lai.
10. **Mechanical Alloying: Fundamentals and Applications** by P. R. Soni.
11. **Recent developments in mechanical alloying**. Rev.Adv.Mater.Sci. 18(2008) 203-211 by C.Suryanarayana.
12. C. Suryanarayana et al./**Materials Science and Engineering** A304–306 (2001) 151–158
13. **The science and technology of mechanical alloying** by C. Suryanarayana, E. Ivanov, V.V. Boldyrev
14. H. Zoz, D. Ernst, R. Reichardt, T. Mizutani, M. Nishida, H. Okouchi, **Metall. 52 (1998) 521-527**
15. **Non-equilibrium Processing of Materials,** by C. Suryanarayana (Pergamon, Oxford, UK, 1999), p.347.
16. **Nanostructured Materials: Processing, Properties and Applications,** C.C. Koch, Second Edition (William Andrew Publ. Co., New York, 2007), p.173
17. Michael Bauccio (2005) ***ASM metals reference book***, ASM International 2005
18. **Preparation of particle dispersion strengthened aluminium by MA,** by T. Takahashi and M. Motoyama, Presented at Powder Metallurgy World Congress, San Francisco, Jan 1992.
19. **Metallographic Etching** by Günter Petzow. American society for metals, Ohio 44073.

APPENDIX

- Magnesium Diffraction Data

35-0821 Wavelength= 1.5405981

Mg

Magnesium

Rad.: CuKa1 λ: 1.540598 Filter: Graph Mono d-sp: Diff.

Cut off: 17.7 Int.: Diffract. I/Icor.:

Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 21, 82 (1984)

Sys.: Hexagonal S.G.: $P6_3/mmc$ (194)

a: 3.20936(11) b: c: 5.2112(3) A: C: 1.6238

α: β: γ: Z: 2 mp:

Ref: Ibid.

Dx: 1.736 Dm: SS/FOM: F_{27} = 76(.0123 , 29)

Color: Dark gray
Peak height intensity. The temperature of data collection was approximately 25.0 C. The sample was obtained from Fisher Scientific Company, Fair Lawn, NJ, USA. It contained a small amount of Mg (O H)2. CAS #: 7439-95-4. Pyrotechnic.
$\sigma(I_{obs})$= ±0.01. Mg type. Tungsten used as an internal stand.
PSC: hP2. To replace 4-770. Mwt: 24.31. Volume[CD]: 46.48.

2_θ	Int	h	k	l
32.194	25	1	0	0
34.399	36	0	0	2
36.620	100	1	0	1
47.829	15	1	0	2
57.375	12	1	1	0
63.058	16	1	0	3
67.314	2	2	0	0
68.633	13	1	1	2
69.998	8	2	0	1
72.495	2	0	0	4
77.823	2	2	0	2
81.528	2	1	0	4
90.415	3	2	0	3
94.315	1	2	1	0
96.820	4	2	1	1
99.187	3	1	1	4
104.236	2	1	0	5
104.501	2	2	1	2
108.267	<1	2	0	4
112.477	1	3	0	0
117.964	2	2	1	3
123.886	1	3	0	2
134.986	<1	2	0	5
136.646	<1	1	0	6
140.739	<1	2	1	4
140.890	<1	3	0	3
147.525	<1	2	2	0

- Iron Diffraction Data

87-0722 Wavelength= 1.54060

Fe

Iron

Iron

2θ	Int	h	k	l
44.765	999*	1	1	0
65.166	115	2	0	0
82.531	175	2	1	1

Rad.: CuKa1 λ: 1.54060 Filter: d-sp: Calculated

Cut off: 17.7 Int.: Calculated I/Icor.: 10.76

Ref: Calculated from ICSD using POWD-12++, (1997)

Ref: Owen, E.A., Williams, G.I., J. Sci. Instrum., 31, 49 (1954)

Sys.: Cubic S.G.: $Im\bar{3}m$ (229)

a: 2.8608(4) b: c: A: C:

α: β: γ: Z: 2 mp:

Ref: Ibid.

Dx: 7.922 Dm: 7.870 ICSD # : 064999

Peak height intensity. PSC: cI2. Calc. density unusual but tolerable. No R value given. At least one TF missing. Mwt: 55.85. Volume[CD]: 23.41.